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HIGH ENERGY MOLECULES
OF HIGH SYMMETRY

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The first phase of this program was an investigation of triquinoyl hydrate (hexaketocyclohexane octahydrate, $C_6H_{16}O_{14}$) which is formed when certain cyclohexane derivatives are treated with cold nitric acid. This ketone hydrate has now been characterized by measurements of its elemental composition, x-ray diffraction pattern, density, infrared and Raman spectrum, carbon thirteen NMR pattern, ultraviolet absorption and fluorescence spectra, ion chromatogram, potentiometric titration curve, solubility, rate of weight loss at several temperatures, heat of decomposition and of combustion, and reactivity toward several different nucleophiles, reducing agents and oxidizing agents. The ketone hydrate is an unusually dense, tightly hydrogen-bonded, acidic, crystalline material which in solution rapidly undergoes dehydration, disproportionation and ring-opening reactions. It may be regarded as a graphite oxide (graphitic acid) having the maximum oxygen-to-carbon ratio.

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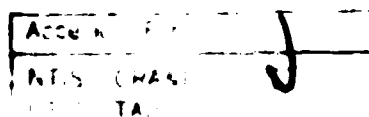DD Form 1473, JUN 86   Previous editions are obsolete.

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Abstract for High Energy Molecules of High Symmetry (con't.)

During the second phase of the program, a series of synthetic routes leading to 2,3,5,6-tetranitro-1,4-diazine (TND) were investigated. Nitrolysis of tetra-carboxydiazine and aminotricarboxydiazine were unsuccessful. Nitrolysis of 2,3-diamino-5, 6-dicarboxy-1,4-diazine and 2,6-diamino-3,5-dicarboxy-1,4-diazine yielded the corresponding diaminodinitrodiazines. A number of oxidation agents and procedures were used on each including peroxytrifluoroacetic acid, peroxytrifluoromethane sulfonic acid and ozone under varing conditions. Both of the diaminodinitrodiazines were impervious to even the strongest oxidizing agents, and TND could not be prepared.

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FIGURES

SUMMARY

The first phase of this program was an investigation of triquinoyl hydrate (hexaketocyclohexane octahydrate, $C_6H_{16}O_{14}$) which is known to be formed when certain cyclohexane derivatives are treated with cold nitric acid. This ketone hydrate has now been characterized by measurements of its elemental composition, x-ray diffraction pattern, density, infrared and Raman spectrum, carbon thirteen nuclear magnetic resonance pattern, ultraviolet absorption and fluoresence spectra, ion chromatogram, potentiometric titration curve, solubility, rate of weight loss at several temperatures, heat of decomposition and of combustion, and reactivity toward several different nucleophiles, reducing agents and oxidizing agents. The ketone hydrate is an unusually dense, tightly hydrogen-bonded, acidic, crystalline material which in solution rapidly undergoes dehydration, disproportionation and ring-opening reactions. It may be regarded as a graphite oxide (graphitic acid) having the maximum oxygen-to-carbon ratio.

The properties observed suggest the following applications for triquinoyl hydrate: cool gas generator, curing agent for epoxy resins, low-loss dielectric, monopropellant ingredient, comonomer for condensation with diamines and source of compressed water for developing pressure in hydraulic systems. In the presence of liquid diepoxides the ketone hydrate is stabilized against gassing; this fact may allow formulation of triquinoyl hydrate compositions which have acceptable shelf life. For the purpose of uncovering new applications it is helpful to think of triquinoyl hydrate as a kind of ice which has very high density (1.92 g/ml), is solid up to about 100 C but instantly melts in the presence of base to release liquid water.

During the second phase of the program a series of synthetic routes leading to 2,3,5,6-tetranitro-1,4-diazine (TND) were investigated. Nitrolysis of tetracarboxydiazine and aminotricarboxydiazine were unsuccessful. Nitrolysis of 2,3-diamino-5,6-dicraboxy-1,4-dazine and 2,6-diamino-3,5-dicarboxy-1,4-diazine yielded the corresponding diaminodinitrodiazines. A number of oxidation agents and procedures were

used on each including peroxytrifluoroacetic acid, peroxytrifluoromethane sulfonic acid and ozone under varing conditions. Both of the diaminodinitrodiazines were impervious to even the stronges oxidizing agents, and TND could not be prepared.

OBJECTIVES

The program was designed to test the concept that polyfunctionality, symmetry, crowding and density in high energy wmolecules will produce an improved balance of oxidizing power against room temperature stability. Initially this involved preparation of a series of cyclic per(hydroxy)hydrocarbons or their ketals in anticipation of converting them to cyclic high energy derivatives (nitro-ketal amine nitrate, amine perchlorate, and others).

During the first year of the program, triquinoyl hydrate was prepared and extensively characterized. It became clear that structures of this type are inherently unstable at ambient temperature, and that they are not good candidates for preparation of energetic derivatives. The limited stability of triquinoyl hydrate is dependent on the symmetry and hydrogen bonding, and when this is disturbed in an attempt to prepare a derivative, rearrangement to rhodizonic acid and open ring structures occurs immediately.

For the second year of the program, the emphasis was shifted to an investigation of the synthesis of symmetrical, energetic, high density heterocyclic compounds. The value of nitro substituted heterocycles such as HMX and RDX has been clearly demonstrated over the years, and synthetic routes to similar structures having higher density and energy can be designed. The objective of the work conducted over the second year of this program has been to prepare and characterize such materials.

1

As starting materials for the preparation of some new, oxygen-rich, high density substances, we chose the per(hydroxylated)cycloaliphatic compounds. The best known member of this series is triquinoyl hydrate (hexaketocyclohexane octahydrate), I, a compound first reported more than one hundred years ago[1], but never derivatized and never fully characterized by modern methods.

$$\text{(OH)}_2 \quad \text{(OH)}_2$$

(OH)2   (OH)2

(OH)2   (OH)2 2H2O

(OH)2   (OH)2
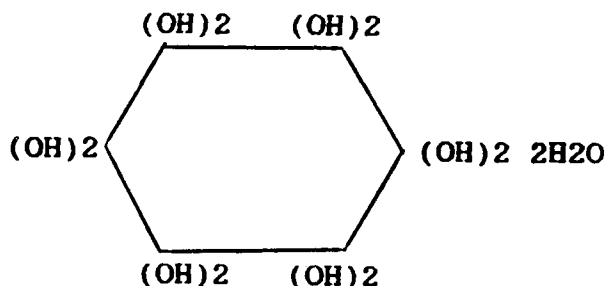
I

The hydroxyl functionality in this molecule, its high oxygen content, its symmetry and its ready availability make this a starting material likely to undergo useful novel reactions.

A large body of literature exists concerning synthesis of high density, high energy materials. After a brief review of that literature, three additional compounds were selected for investigation under this program. Those three materials and the estimated properties of each is shown in Figure 1. Selection of these materials for synthesis is based on the work conducted by Don Levins (currently at CSD) under an AFRPL contract at SRI International.[2] During the course of that work, Don Levins prepared a compilation of several thousand high energy compounds which was reduced to about 200 compounds of interest. The first two compounds shown were

investigated under that program. The rationale for selection of the compounds shown is based on the probability of a successful synthesis and the fact that they meet the criteria for materials to be investigated on this program.
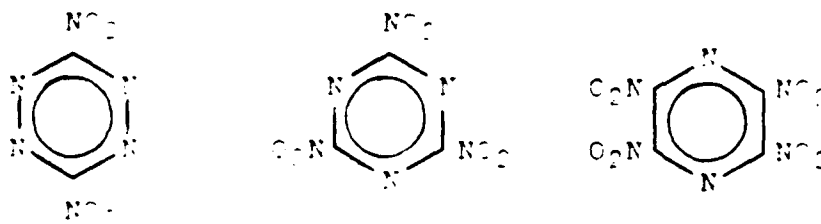
Acronym	DNTT	TTZ	TND
Estimated	2.0	2.0	2.0 density
Oxygen	+1.2	+1.4	+1.5 Balance*
Estimated heat of formation	1U4	68	59

----

* Weight % based on conversion to CO

Figure 1. Candidate Compounds

2,3,5,6-Tetranitro-1,4-diazine (TND) was selected as the first compound to be prepared because the intermediate to be used in the synthetic routes are well known,[3,4,5,6,7] there are several alternative routes available, and investigation of those routes could help to provide insight into the complicated processes involved in amine oxidation. In the earlier efforts to prepare 3,6-dinitro-1,2,4,5-tetrazine (DNTT) and 2,4,6-trinitro-1,3,5-triazine (TTZ), the primary problems were in synthetic steps involving the oxidation of amines. It was anticipated that knowledge gained in the synthesis of TND would make it possible to prepare DNTT and TTZ.

3

DISCUSSION

PREPARATION AND PROPERTIES OF TRIQUINOYL HYDRATE

The structure and the known properties of triquinoyl hydrate are so unusual that we have decided to obtain several samples of this material and characterize them by a variety of instrumental methods before proceeding to the study of reactions and uses. The samples and their properties are described in this section.

Preparation

Triquinoyl hydrate has been reported to be the reaction product obtained by treating several hexa-substituted cyclohexane or benzene derivatives with cold, concentrated nitric acid (Figure 2). As starting materials one may use inositol (a readily available natural product), rhodizonic acid (obtainable from the reduction of carbon monoxide with potassium metal) or tetrahydroxyquinone (accessible from the self-condensation of glyoxal). The variety of suitable starting materials and their low cost suggest that triquinoyl hydrate might be made available on a large scale if needed.

A laboratory preparation developed at the National Bureau of Standards has been described in detail[8]. This preparation has now been repeated and shown to yield a colorless crystalline product with the expected melting point, infrared spectrum and elemental composition (Table 1). Research quantities of the compound ("hexaketocyclohexane octahydrate, 97%") are also available from Aldrich Chemical Company (Aldrich 12,856-2, Lot 1701 ML) and from other suppliers. The inorganic content and the carbon/hydrogen ratio in the Aldrich product (Table 1) are both higher than desired but can be improved by recrystallization from nitric acid/methanol by the NBS procedure (Table I).

4
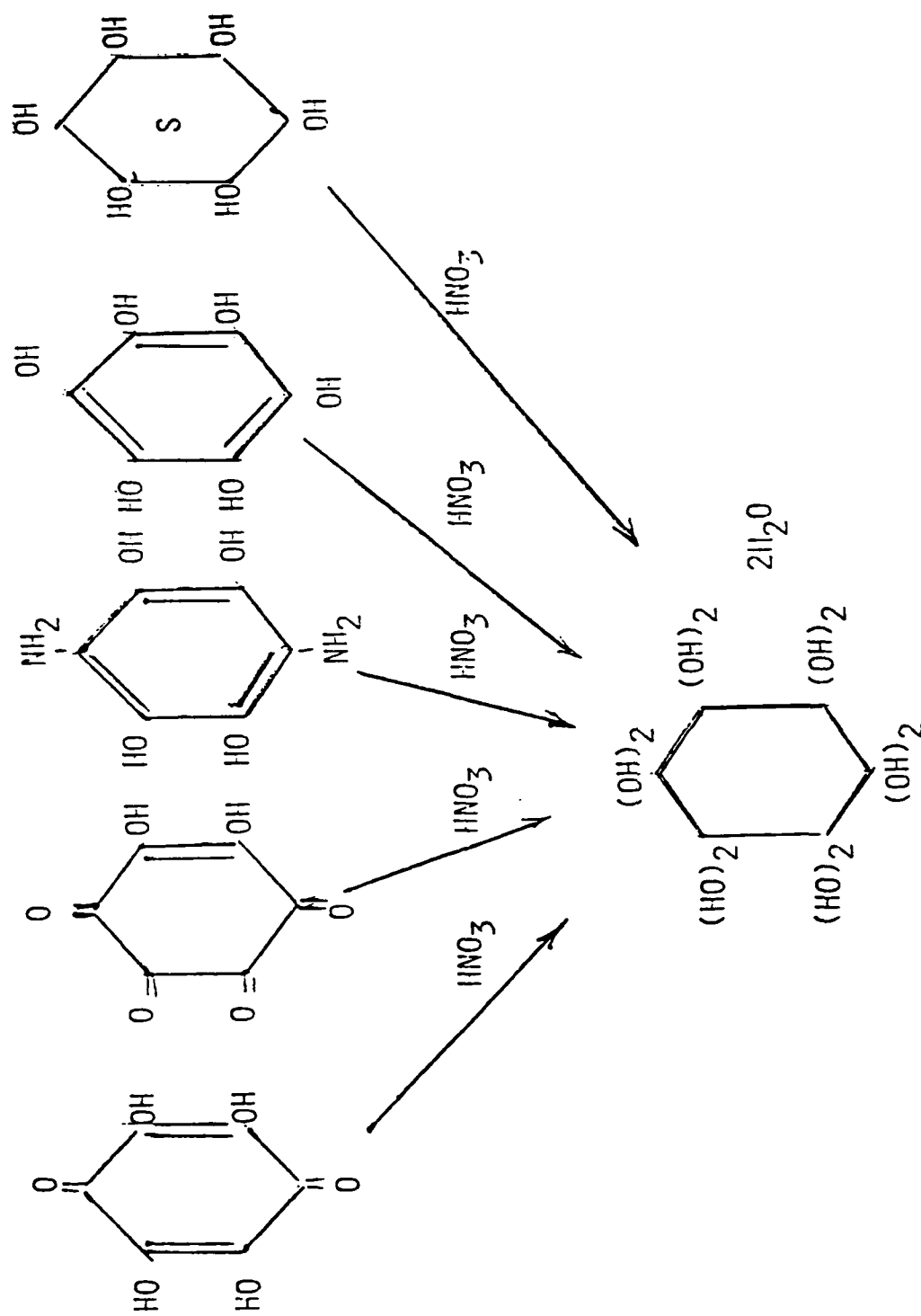
Figure 2. Preparation of Triquinoyl Hydrate

Table 1. Elemental Composition of Triquinoyl Hydrate[a]

	Theoretical Composition	Sample prepared in this work by Bureau of Standards Method[c]	Aldrich Lot 1701 ML[d]	Aldrich Lot 1701 ML after recrystallization by Bureau of Standards Method[e]
Carbon, %	23.05	23.20	24.24	23.17
Hydrogen, %	5.17	5.24	4.99	5.16
Oxygen, %	71.78	71.56[b]	--	--
Nitrogen, %	0	--	<0.0042	--
Ash, %	0	0.05	0.61	0.34

---

a) Elemental analyses performed at Galbraith Laboratories, Knoxville, TN.
b) By difference.
c) Our sample number III-123, colorless plates.
d) Brown powder, 97% purity according to supplier.
e) Our sample number IV-57, colorless plates.

In a patent[9] there is a claim for an improved, high-yield method for preparing the ketone hydrate. The product obtained is described as stable at 100 C and cyclohexane-soluble. Later in the present report it will be shown that these are not characteristics of triquinoyl hydrate, however. The patent claims are therefore regarded as suspect.

Melting Point

When heated rapidly on a melting point block the samples of Table 1 melt at 98-100 C. There is considerable frothing at the melting point; water and carbon dioxide are evolved. Because decomposition is rapid at 100 C, the melting point is not a reliable method for characterizing triquinoyl hydrate.

Infrared Spectrum

The spectrum of triquinoyl hydrate is shown in Figure 3. In the spectrum there are hydroxyl stretch absorptions, no carbon-hydrogen stretch bands, some carbon-oxygen stretch bands and in addition bands at 890 and 1280 cm^{-1} where many other cyclohexane derivates are known to absorb.[10] The spectrum is in good agreement with that reported in the literature[11] and is not changed significantly by washing the sample three times with water (to remove 31% of the sample). Recrystallization from nitric acid/methanol also does not significantly affect the spectrum.

A striking feature of this spectrum is the absence of strong absorption in the carbonyl region as well as in the carbon-hydrogen stretch region. It was pointed out by Person and Williams[11] that the spectrum supports the fully hydrated structure containing geminal dihydroxy groups (structure I of the introduction).

The far infrared spectrum of triquinoyl hydrate (Figures 4 and 5) consists of several narrow bands bearing a resemblance to the bands of ice. Large contributions to the heat capacity of triquinoyl hydrate are presumably made by the low frequency, ice-like oscillations.
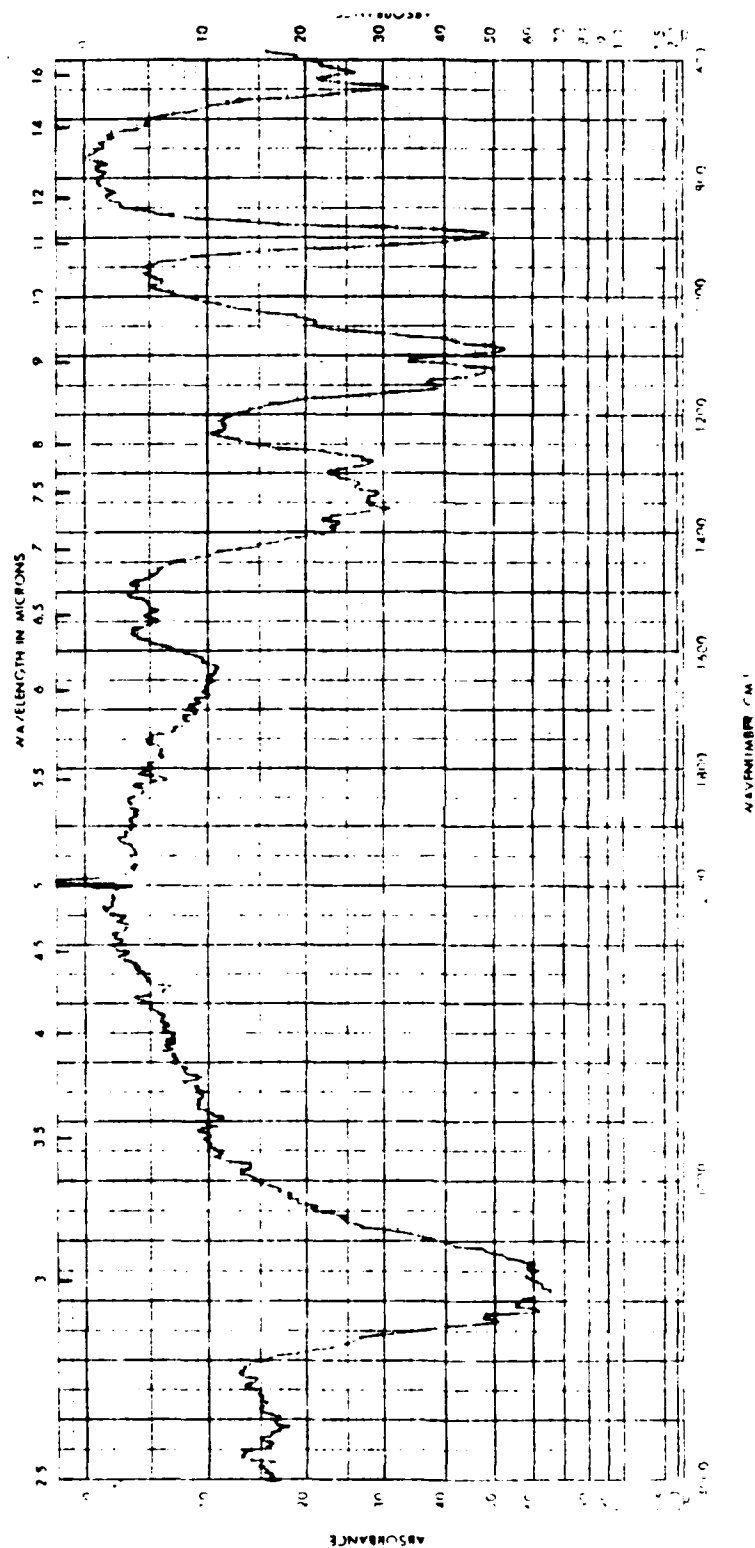
Figure 3. Infrared Spectrum of Triquinoyl Hydrate (Aldrich Lot 1701 ML) in KBr Pellet

8

Figure 4. Far infrared spectrum of triquinoyl hydrate (sample III-123) in polyethylene pellet.

Peaks (wavenumber): 121.686, 134.370, 154.250, 173.733, 208.193, 225.650, 251.162, 260.657, 281.440, 306.196, 322.384, 422.387

WAVENUMBER axis: 50, 125, 200, 275, 350, 425, 500

ABSORBANCE axis: .000, .022, .044, .066, .088, .110, .132

32

6

Figure 5. Far infrared spectrum of triquinoyl hydrate (sample III-123) in polyethylene pellet.

NICOLET 60SXB FTIR
UNITED TECHNOLOGIES
01/10/85 10:20:34
125.07 SEC. MEAS. TIME

APT = BL
AFN = HG
GAN = 64
HPS = 0
LPS = 1
NDP = 4096
NPO = 200
NPT = 1024
NSD = 128
NSK = 700
NTP = 8192
SGH = 8
SGL = 8
SSP = 2
VEL = 70
DET = 2
NSB = 128

33

10

We are indebted to Bob Rosenthal, Nicolet Instruments, Madison, Wisconsin for the far infrared data.

Raman Spectrum

Bands in the Raman spectrum of triquinoyl hydrate (Figure 6) do not in general have an exact counterpart in the infrared. The strongest Raman band (690 cm^{-1}) clearly has no infrared counterpart; this band isbelieved to be the symmetrical ring-breathing band. The frequency of this band is lower than the corresponding ring-breathing bands in the five membered and four-membered ring compounds.[12]

Although good Raman data were obtained on crystalline triquinoyl hydrate, water solutions of this material proved too strongly fluorescent to permit spectroscopy on the solution. The fluorescence of the material is discussed in a separate section of this report.

We are indebted to Mark Andersen, McCrone Associates, Chicago for the Raman data.

Ultraviolet Spectrum

In spite of the fact that the infrared spectrum does not support the free ketone structure, an aqueous solution of the ketone hydrate absorbs in the ultraviolet about as expected for free ketone (Figure 7; $\lambda_{max} = 267$ nm). The conclusion, already reached b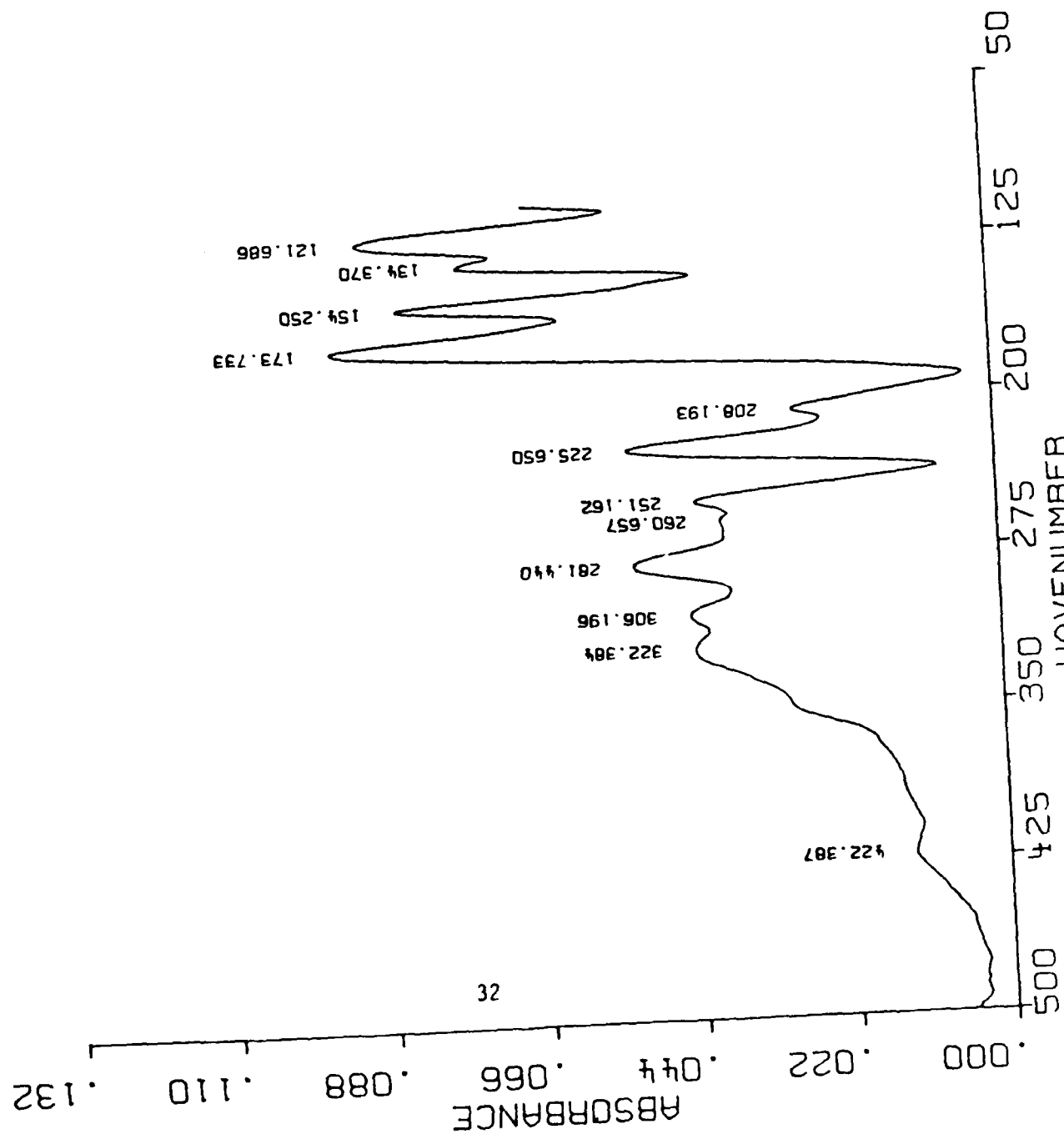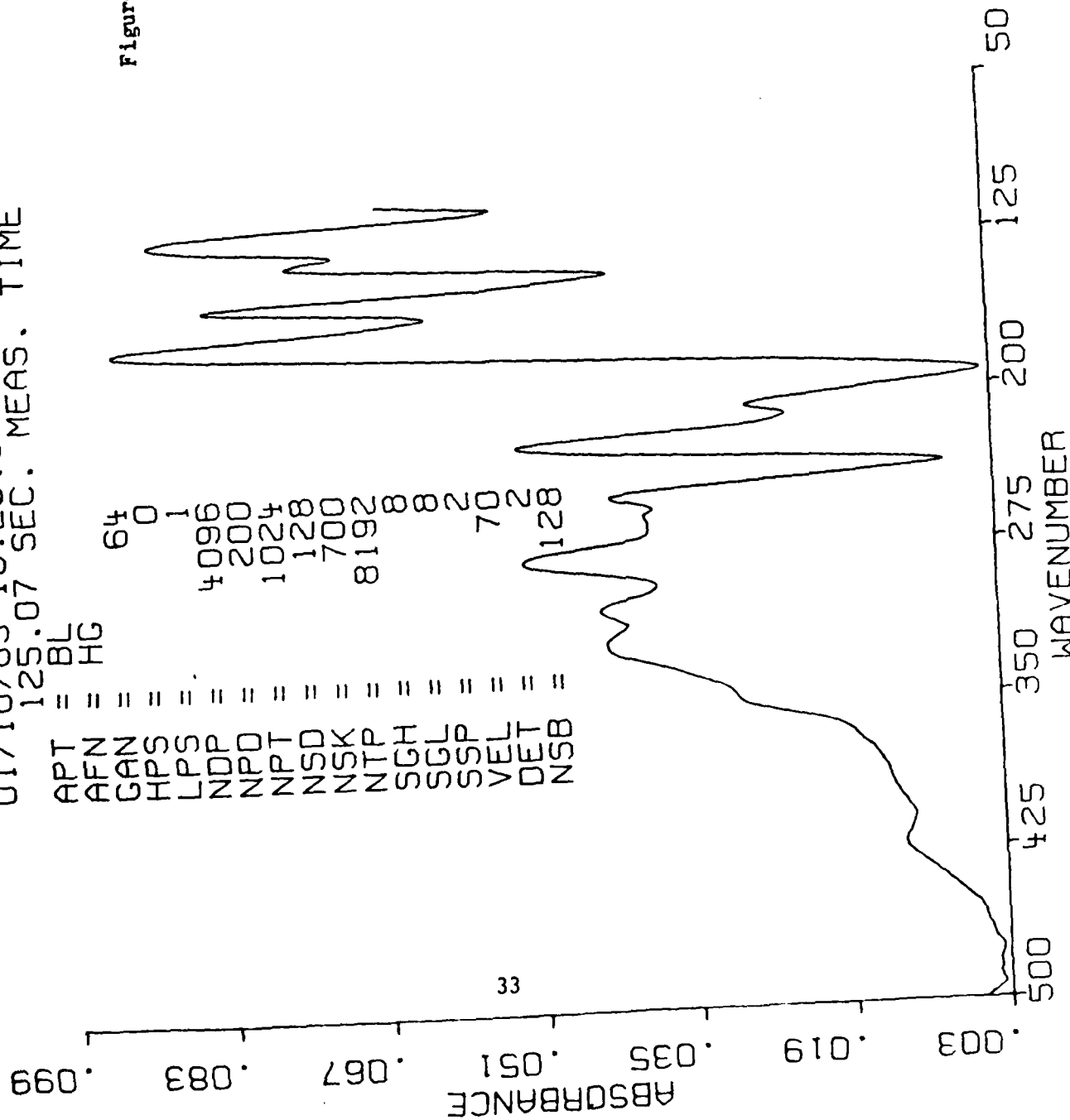y others, is that dehydration occurs when the fully hydrated structure is dissolved in water. If it is assumed that the absorptivity of the carbonyl groups in this solution is the same as in acetone then the observed absorbance would indicate that there are about three ketone groups per mole of triquinoyl hydrate in solution, i.e., that most of the dissolved material has the structure II

II

11

Figure 6. Raman Spectrum of Triquinoyl Hydrate
(Pure Sample III-123 of Table 1)
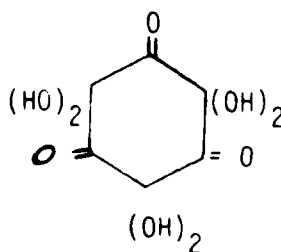
Figure 7. Ultraviolet absorption spectrum of triquinoyl hydrate. Concentration: 0.3006 grams in 100 ml of 2N sodium chloride. Sample prepared by NBS method (Table 1).
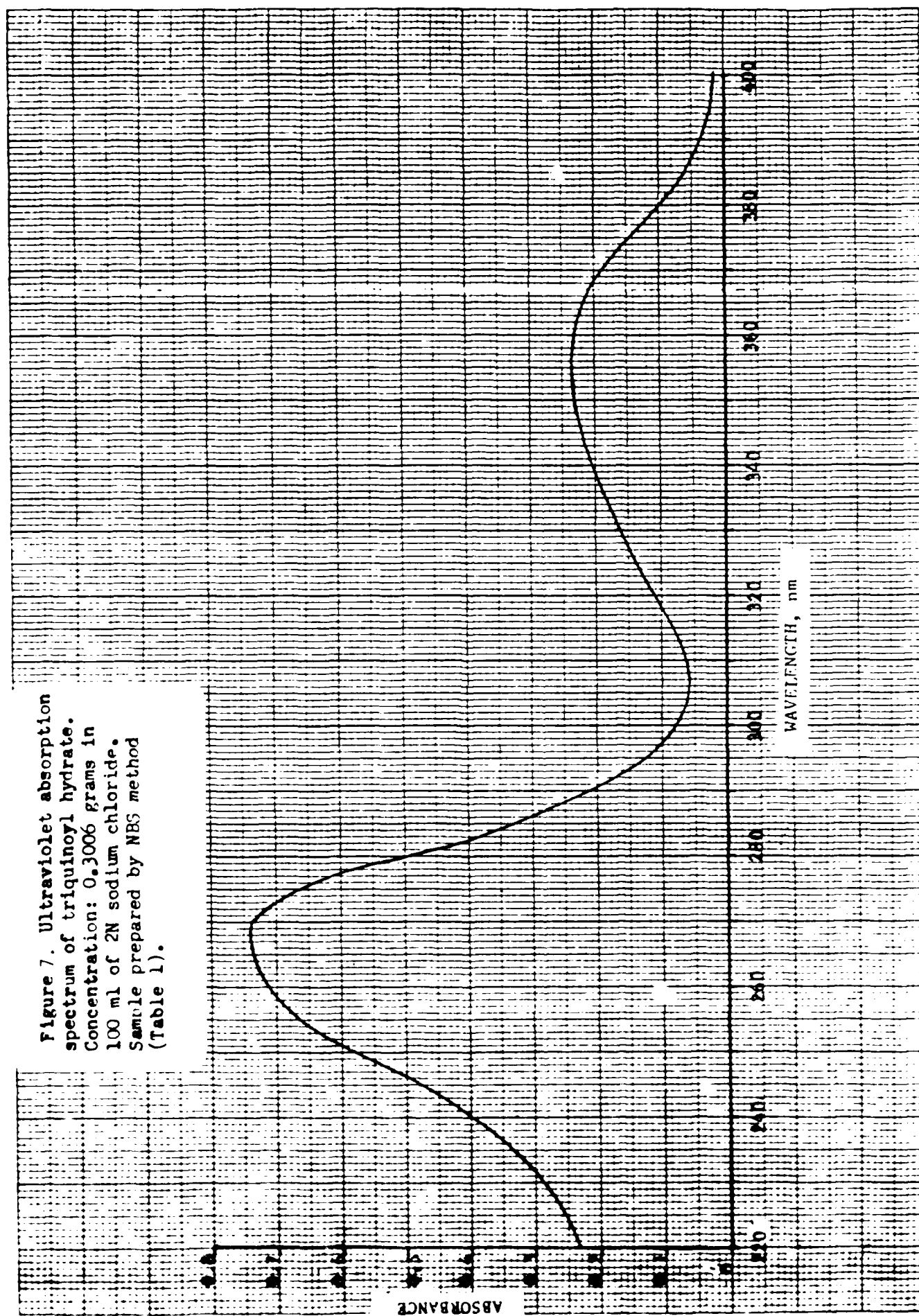
The absorptions at longer wavelengths (355 nm) show that the aqueous solution contains conjugated, more highly dehydrated structures and that structure II is not the only (or even the major) dehydration product present. The composition of the aqueous solution is discussed further in the NMR section of this report.

Very pure samples are required in order to record the ultraviolet spectrum of triquinoyl hydrate. The colored impurities and decomposition products absorb strongly in the ultraviolet and obscure the 267 nm maximum characteristic of the pure substance. The spectrum of Figure 7 is in excellent agreement with National Bureau of Standards data.[8]

Fluorescence Spectrum

Crystalline colorless ketone hydrate does not fluoresce visibly when irradiated with a 254 nm lamp. In aqueous brine solution, however, it fluoresces measurably in the visible (Figures 8 and 9). This provides further evidence of the presence of free ketone(s) in the solution. Impurities in commercial triquinoyl hydrate (Aldrich Lot 1701 ML) are powerfully fluorescent and may be excited with visible light.

When deposited on fluorescent, doped silica, thin layer chromatography plates, triquinoyl hydrate displays a pink fluorescence when irradiated with a 254 nm lamp. The fluorescence is not characteristic of triquinoyl hydrate, however; acidic substances in general (including hydrochloric acid) cause these plates to fluoresce in the pink.

Paul Spink, Perkin-Elmer Corporation, Mountain View, California provided the fluorescence spectra of Figures 8 and 9.

X-ray Diffraction

The crystal structure and molecular dimensions of triquinoyl hydrate have never been reported in spite of the fact that the symmetry of the molecule should make interpretation of the diffraction pattern simple. To prepare crystals suitable for single-crystal diffraction, some of Aldrich

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Figure 8. Fluorescence spectrum of triquinoyl hydrate

1701 ML: Aldrich lot 1701 ML as received 32 mg/10 ml 2N NaCl

IV-57: Aldrich lot 1701 ML water-washed and recrystallized 30 mg/10 ml 2N NaCl

Perkin-Elmer LS-5 spectrofluorimeter

254 nm excitation

MAX=4.69

MIN=-0.55

<--1701 ML

IV-57-->

Emission wavelength, nm

.15
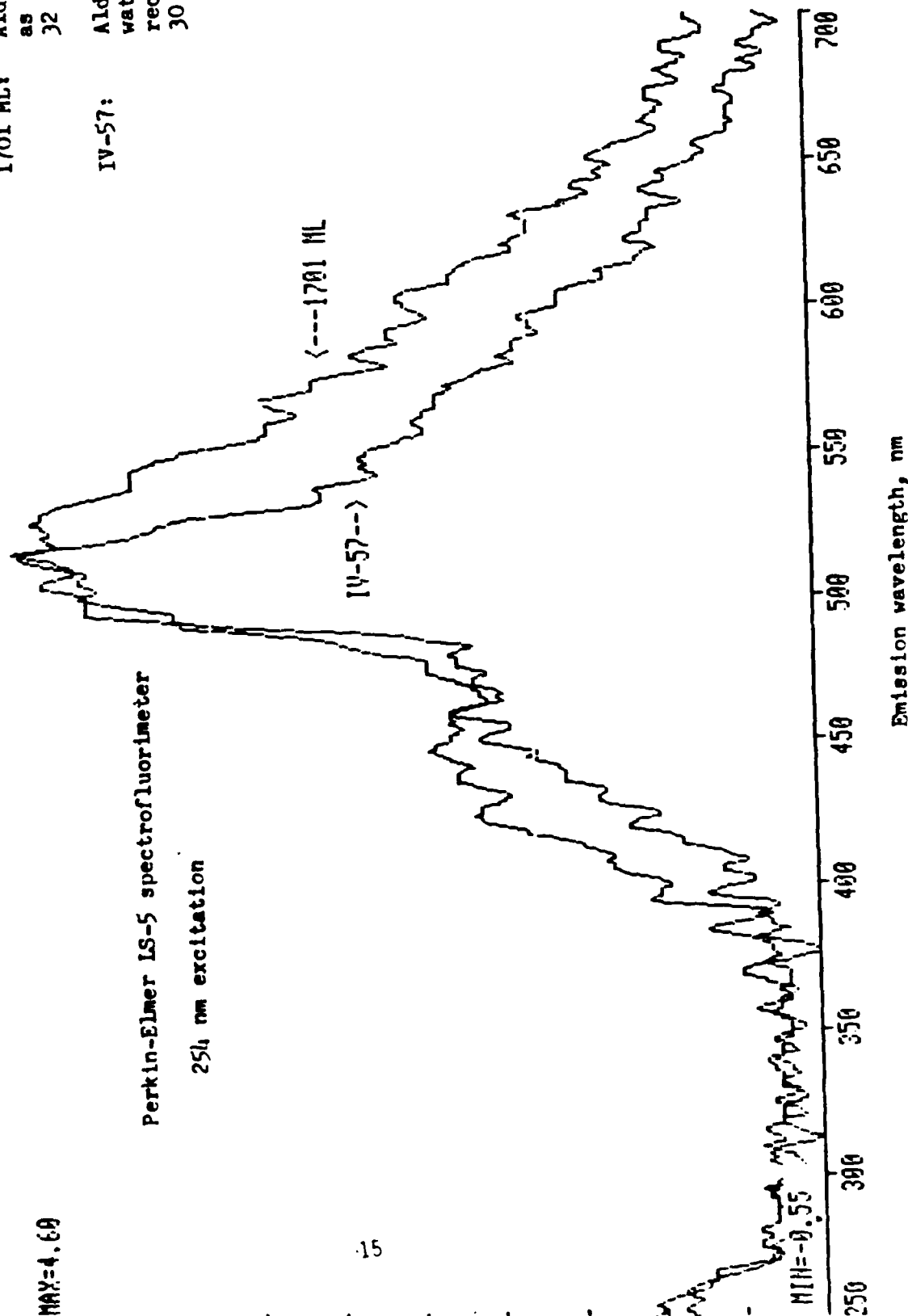
Figure 9. Fluorescence spectrum of triquinoyl hydrate at three excitation wavelengths.

MAX=7.49

TRIQUINOYL HYDRATE IN 2N NaCL
IY-57 30MG IN 10ML
SLITS 15/10
LS-5
11/22/85

MIN=-0.45

<--276NM

267NM-->

254NM-->

Wavelength, nm

16
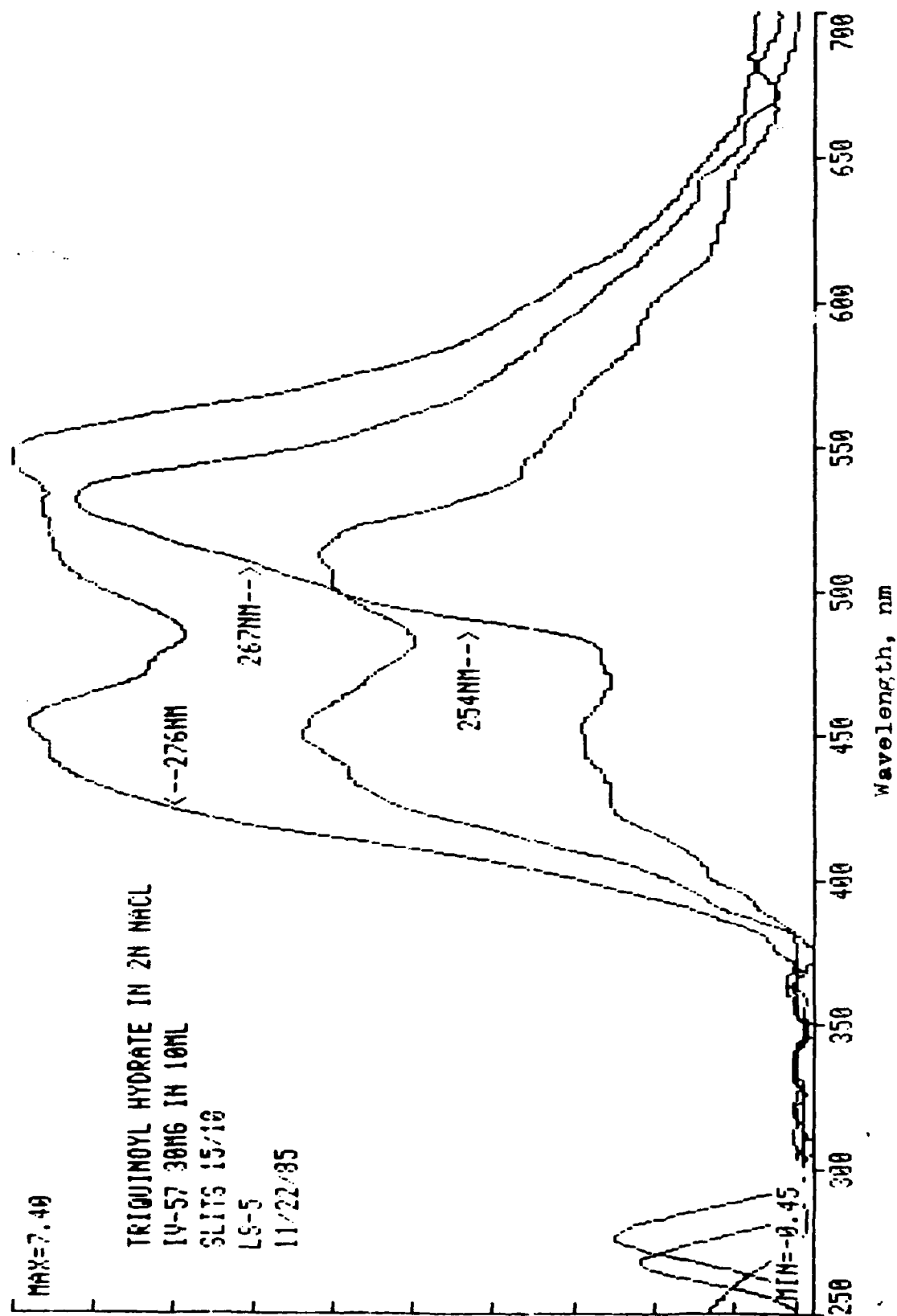
Lot 1701 ML was recrystallized from methanol/acetone/nitric acid as suggested by Fatiadi, et al[8] (Bureau of Standards method; sample III-127). This gave some nearly colorless plates about 0.1mm in thickness. When examined under the polarizing microscope some of these crystals appeared to be uniform as to refractive index and free of visible flaws. They had density 1.9 g/ml as determined by sink-or-float observations in solutions of known density. The crystals therefore appeared good candidates for x-ray diffraction and were submitted to Dr. W. T. Pennington, Molecular Structure Corporation, College Station, Texas for a structure determination.

The ORTEP representation of the molecule resulting from the Molecular Structure Corporation study shows that there is a center of symmetry at the center of the cyclohexane ring; each of the O-H bonds has one matching anti-parallel O-H bond at the opposite end of the molecule. Unlike the planar ring in the corresponding cyclobutane derivative[13], the cyclohexane ring in $C_6H_{16}O_{14}$ has the non-planar, chair conformation.

All of the hydrogen atoms participate in hydrogen bonding. The resulting packing of the molecules within the crystal is very tight and is difficult to represent in two dimensions. An attempt to do so is the drawing of Figure 10. The exceptionally tight packing is reflected also in the calculated density of the crystal, 1.92 g/ml. This density is not as high as that of the corresponding cyclobutane derivative[13], 1.98 to 2.00 g/ml, but is far higher than for the typical monocyclic carbon-hydrogen-oxygen compound.

The connectivity of the hydrogen-bonding in the triquinoyl hydrate crystal is shown in Figure 11. This pattern is derived from the x-ray diffraction pattern by applying the following criterion: If the O···H separation in the crystal is 0.02-0.03 nm less than the sum of the van der Waals radii, then a strong hydrogen bond exists at O···H. By applying this test to the x-ray data the three types of hydrogen-bond (tri-, di- and monofunctional) shown in Figure 11 can be identified.
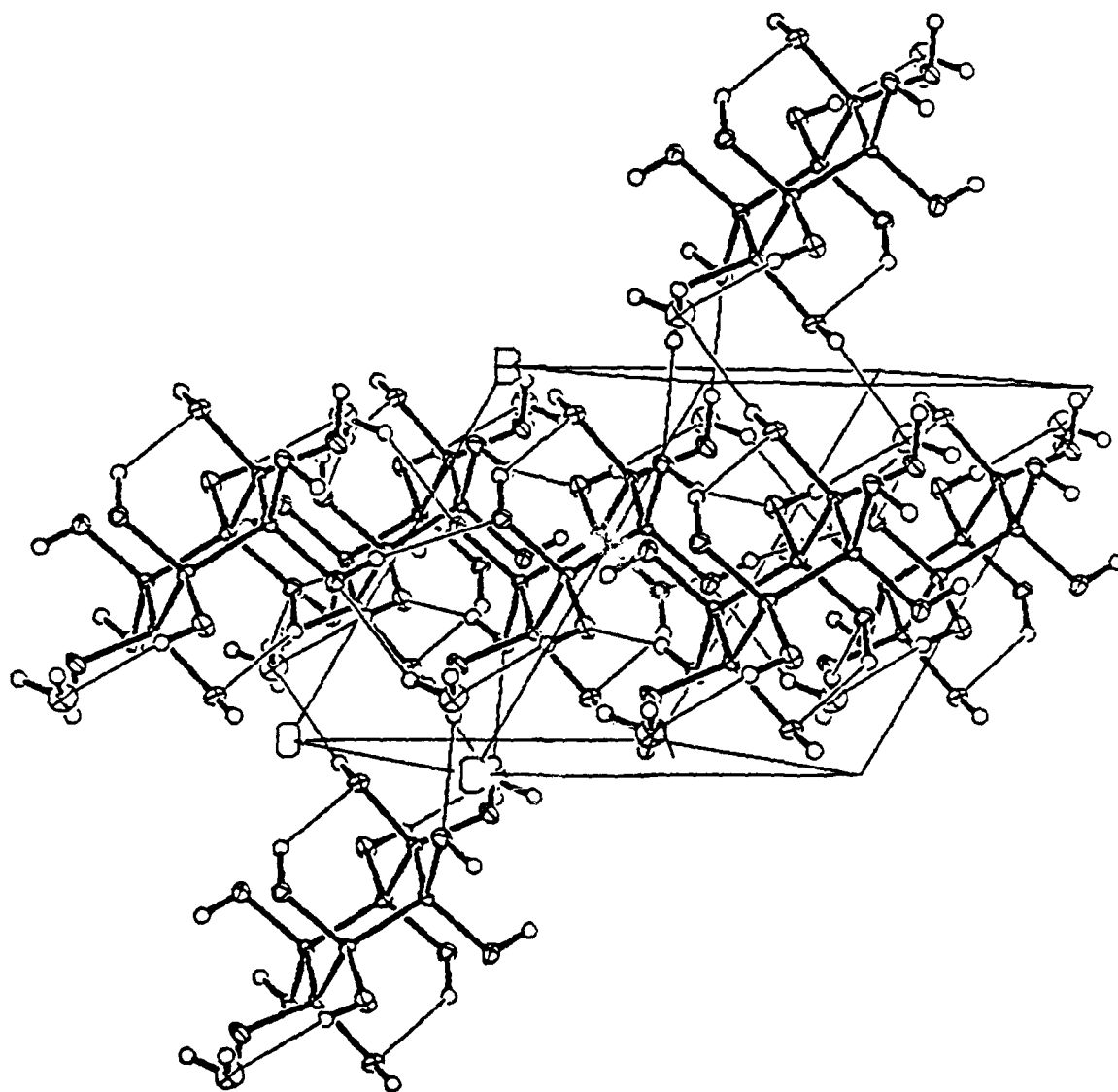
Triclinic space group, P1-bar, unit cell volume 269.5(3) Å³
calculated density 1.39 g/cm³
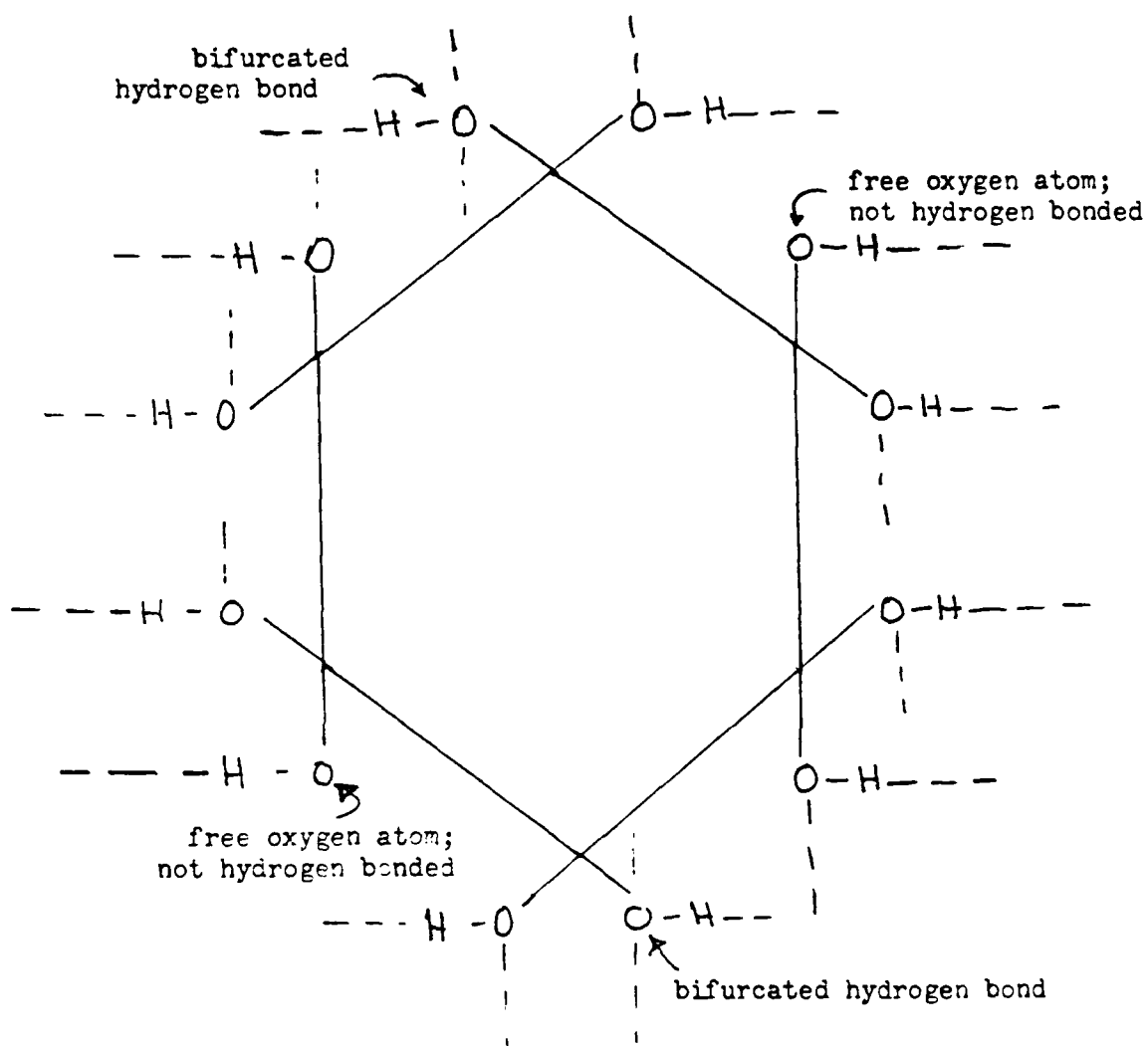
Figure 10. Unit cell of triquinoyl hydrate

Figure 11. Hydrogen bonding pattern in triquinoyl hydrate crystal. (Intramolecular hydrogen bonding occurs only at the bifurcations.)

It is useful to estimate the additional bond energy provided by the hydrogen bonds in this crystal. Since there are sixteen hydrogen bonds associated with each $C_6H_{16}O_{14}$ molecule and each contributes about 2 to 6 kcal/mole to the bonding[14], the total bond energy contributed by hydrogen bonds is 32-96 kcal/mole! This is the energy equivalent of additional covalent carbon-carbon bond in the molecule. In an energy sense then, the bonding in this crystal is that of a bridged-ring, polycyclic or polymeric, ring-in-chain compound. The high density of the crystal also reflects this additional bonding energy.

NMR Pattern

When dissolved in two normal sodium chloride solution containing 10% added deuterium oxide, triquinoyl hydrate gave the ^{13}C NMR pattern shown in Figures 12 and 13. The group of signals near 100 ppm are attributable to sp^3 carbons; the three signals at 143 ppm, 191 ppm and 202 ppm are attributable to carbonyl carbons. This spectrum supports the conclusion derived from the ultraviolet spectrum, namely, that the $C(OH)_2$ groups lose water when the ketone hydrate is dissolved in brine. At least sixteen sp^3 signals appear in the spectrum; sixteen is the number expected for dehydration to yield a mixture of cyclic monoketone, all three isomeric diketones and all three isomeric triketones (Figure 14). The spectrum indicates dehydration at least through the triketone level and possibly further. That the carbonyl carbon pattern is not as complex as calculated in Figure 14 is perhaps due to coincident carbonyl signals from two or more ketones.

From a polarographic study it was concluded that triquinoyl hydrate in water solution is fully hydrated[15]. The NMR results show that this conclusion is only approximately correct; unhydrated carbonyl groups are clearly present.

104   102   100   98   96
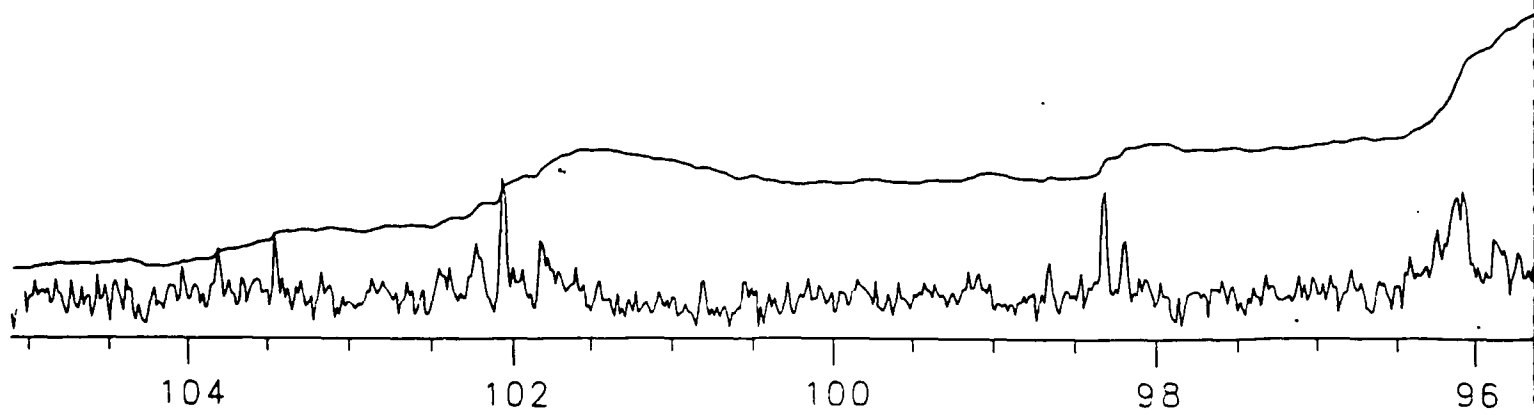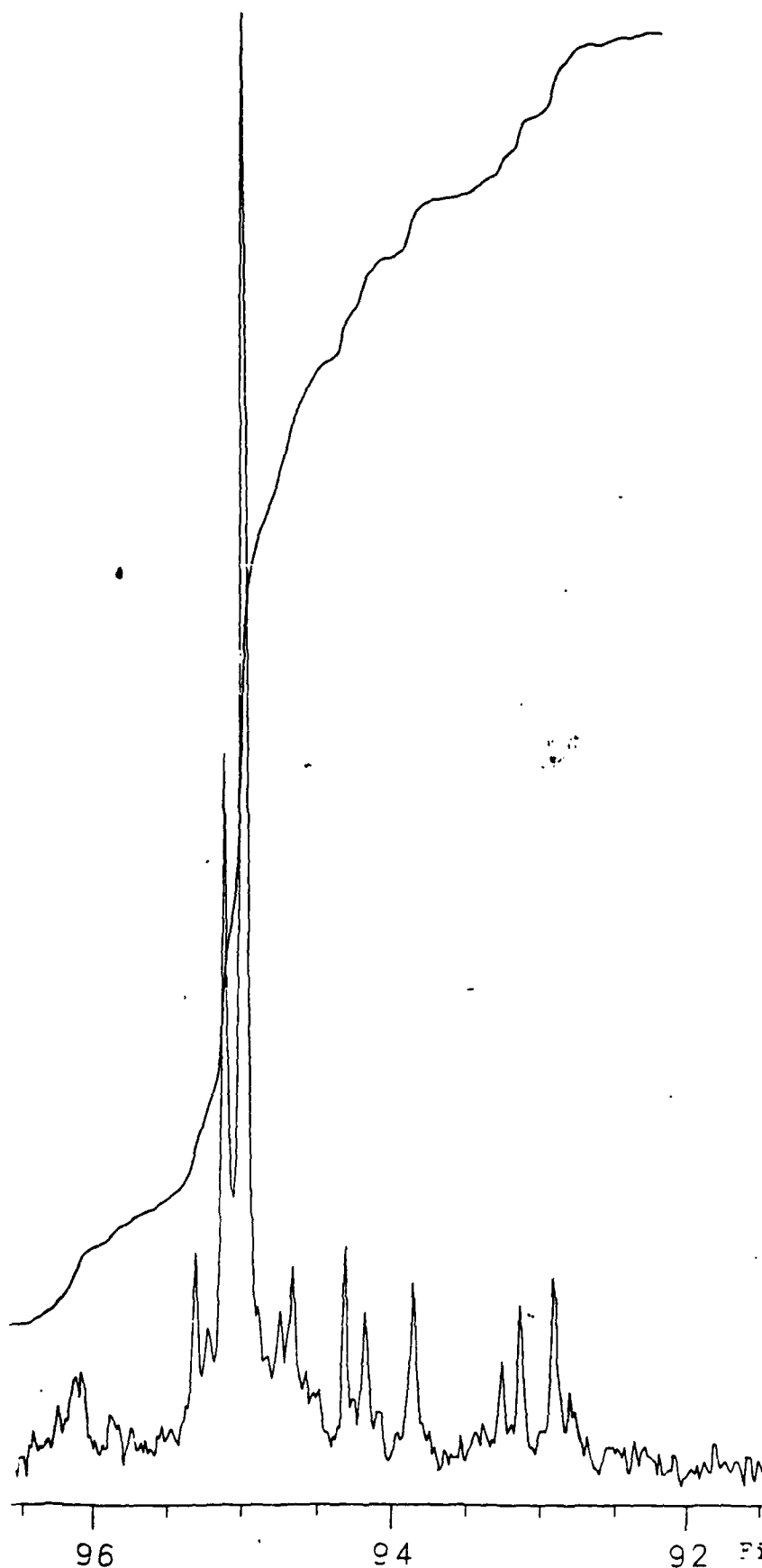
GE NMR
QE-300

UT.601
16DEC85

IV-57 TH
2N NACL H2O+ 10%D2O

OPERATOR: GE NMR

ONE PULSE SEQUENCE

P2   =   7.38 USEC

D5   =   181.00 MSEC

ACQ. TIME   =   819.20 MSEC

NO. OF ACQS. =   40000
DATA SIZE   =   32768
LINE BROADNG =   1.00 HZ
SPIN RATE   =   0 RPS

OBSERVE:
 FREQUENCY =   75.484146 MHZ
 SPEC WIDTH= 20000 HZ
 GAIN   =   55 dB

DECOUPLER: STANDARD MODULATION
 FREQUENCY = 4.000 PPM
 POWER   = 2940/ 3100
 HIGH POWER ON
 HIGH POWER OUTPUT (0-63 DB) =   58

PLOT SCALE:
      30.33 HZ/CM
       .4019 PPM/CM
  FROM   105.11
    TC   91.46 PPM

Figure 12. Carbon thirteen NMR pattern of triquinoyl hydrate in brine solution (sample IV-57); sp^3 carbon region

96   94   92
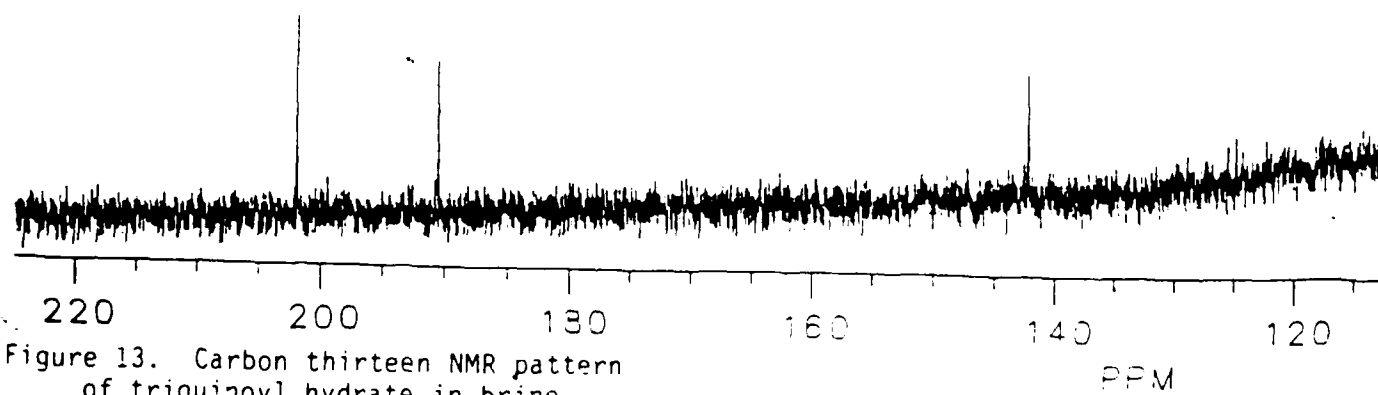
Figure 13. Carbon thirteen NMR pattern
   of triquinoyl hydrate in brine
   solution (sample IV -57)

GE .NMR
QE-300

UT.601
16DEC85

IV-57 TH
2N NACL H2O+ 10%D2O

OPERATOR GE NMR

ONE PULSE SEQUENCE

P2   =   7.38 USEC

DS   =   181.00 MSEC

ACQ. TIME   =   819.20 MSEC

NO. OF ACQS   =   40000
DATA SIZE   =   32768
LINE BROADNG =   1.00 HZ
SPIN RATE   =   0 RPS

OBSERVE
 FREQUENCY =   75.484146 MHZ
 SPEC WIDTH= 20000 HZ
 GAIN   = 55 +8

DECOUPLER STANDARD MODULATION
 FREQUENCY = 4.000 PPM
 POWER   = 2940/ 3100
HIGH POWER ON
HIGH POWER OUTPUT (0-63 DB) =   58

PLOT SCALE
      413.06 HZ/CM
        5.4722 PPM/CM
  FROM   224.99
    TO   38.96 PPM

22
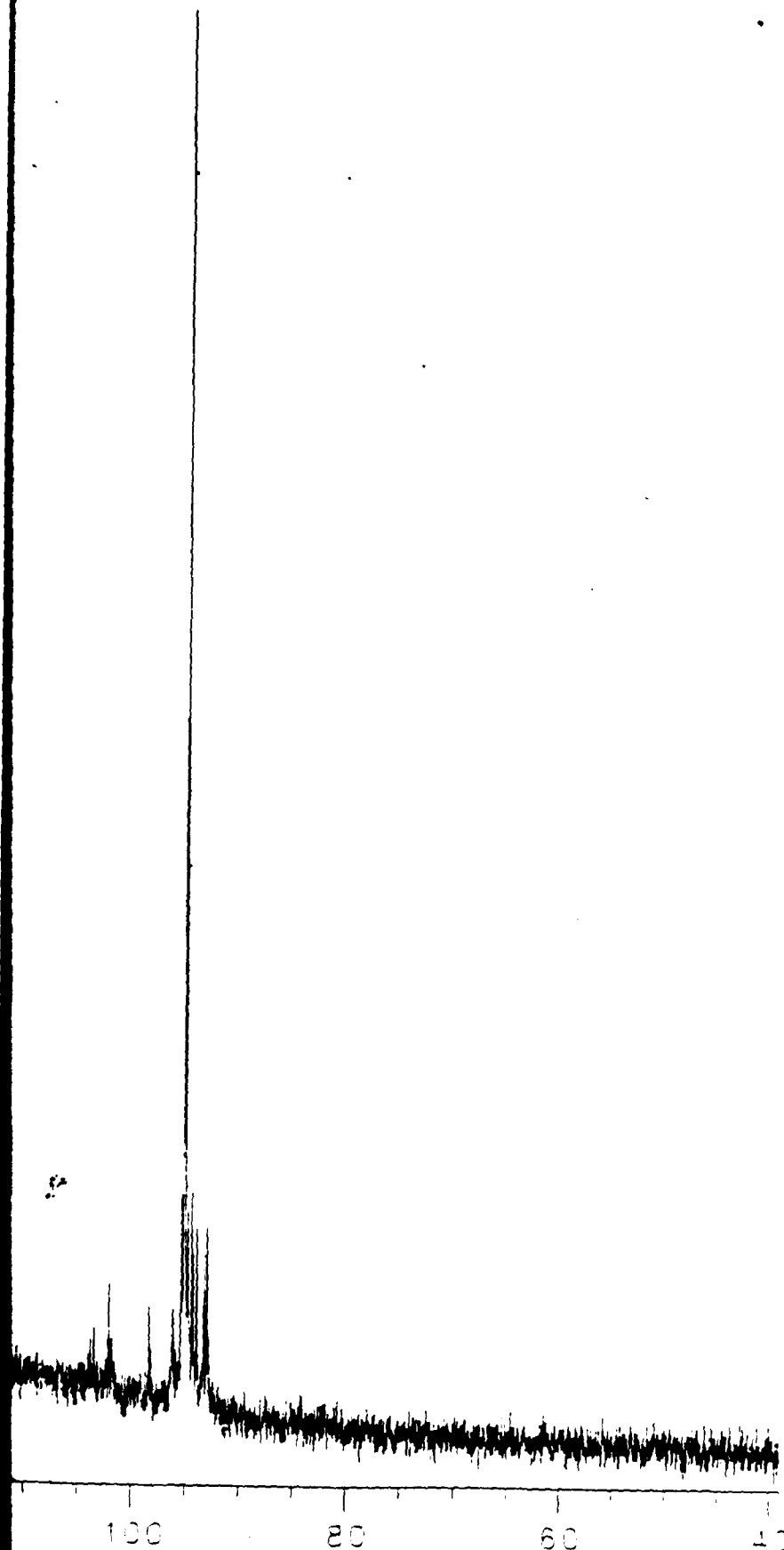
SP3 signals expected	Carbonyl signals expected
1	0
3	1
2	1
3	1
1	1
2	2
3	3
1	1

Figure 14. Triquinoyl Hydrate Dehydration Products

Differential Scanning Calorimetry

When heated in a differential scanning calorimeter, the ketone hydrate first undergoes a large endothermic change, then a small exothermic one and finally a very small endothermic change (Figure 15). The first endotherm is quite large, larger even than the endotherm for melting ice (80 cal/gm). The magnitude of this first change is doubtless the net result of simultaneous melting (endothermic), dehydration or decarboxylation (possibly exothermic) and vaporization of water (highly endothermic). All of these processes involve the rupture of multiple hydrogen bonds, of course, and a large endotherm is expected from that source alone.

When triquinoyl hydrate is warmed from liquid nitrogen temperature to room temperature in the scanning calorimeter no transitions (heat capacity discontinuities) are detected. The hydroxyl groups of triquinoyl hydrate evidently do not undergo the flip-flop motion found in other polyhydroxylic compounds.[16] The sharp x-ray diffraction pattern observed for room-temperature triquinoyl hydrate seems consistent with the differential scanning calorimeter results.

Heat of Combustion

A sample of Aldrich Lot 1701 ML was submitted to the coal testing laboratory at Galbraith Laboratories, Knoxville, Tennessee for determination of heat of combustion. The measured heat is 1886 BTU/lb, which corresponds to 327 kcal/mole or 1.1 kcal/gm. A comparison of this heat with the corresponding handbook values for cyclohexane and for inositol is shown in Figure 16. The effect of mono-hydroxylation and di-hydroxylation of each carbon are similar; the introduction of the first six and second six hydroxyl groups both reduce the molar heat of combustion of cyclohexane by about 300 kcal/mole. On an equal volume basis, however, the effect of increasing the hydroxyl content is not as large (Figure 16).
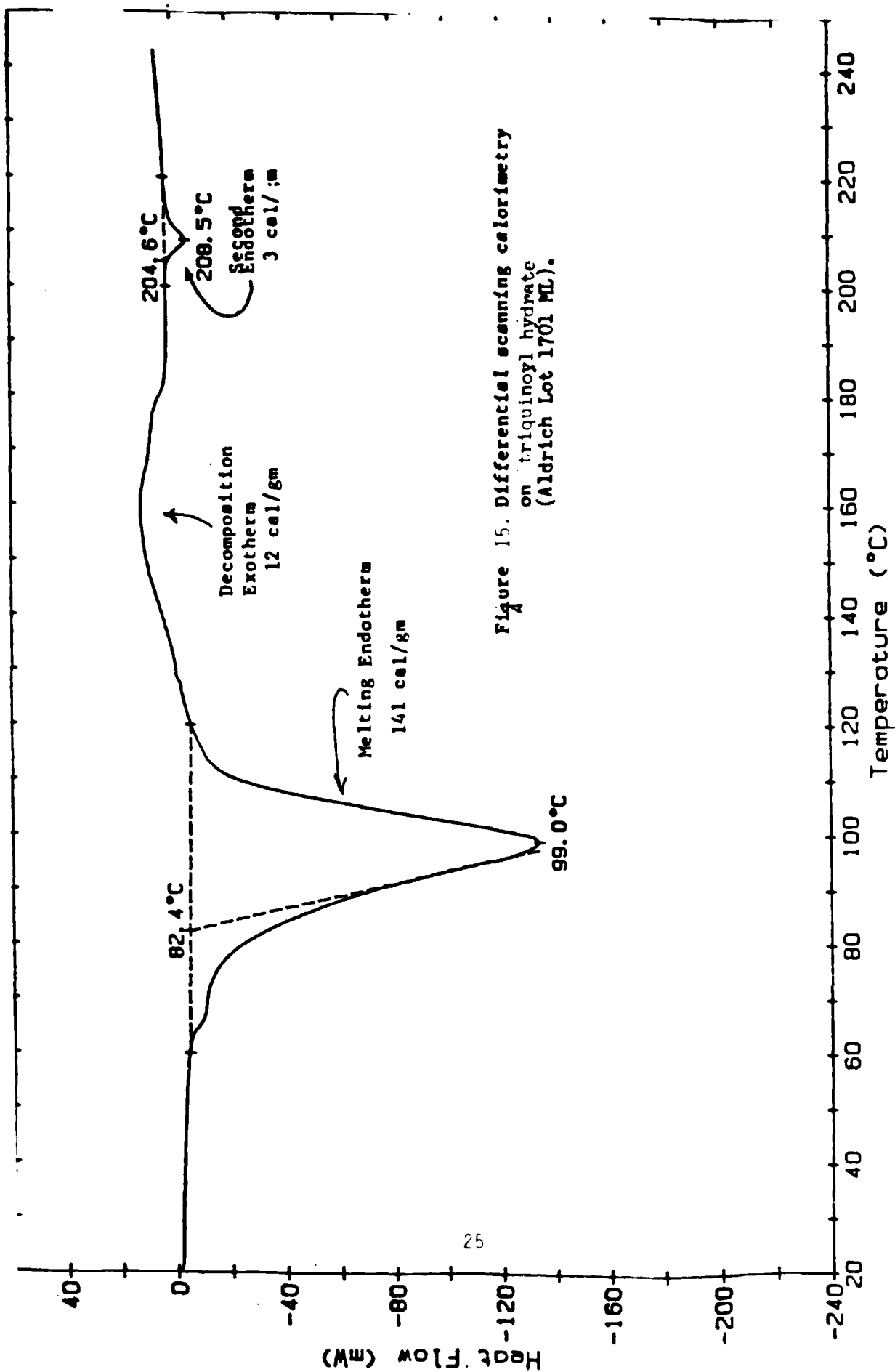
Figure 15. Differential scanning calorimetry on triquinoyl hydrate (Aldrich Lot 1701 ML).

Cyclohexane (liquid)	Inositol (solid)	Triquinoyl Hydrate (solid)
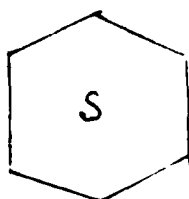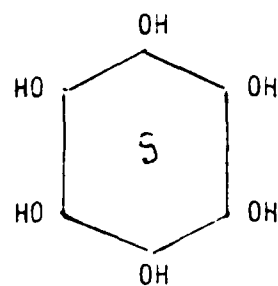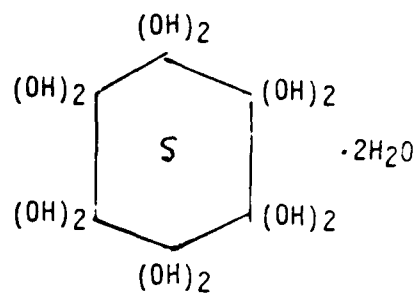
Cyclohexane (liquid)	Inositol (solid)	Triquinoyl Hydrate (solid)
937 kcal/mole	661 kcal/mole	327 kcal/mole
11 kcal/g	3.7 kcal/g	1.1 kcal/g
8.5 kcal/ml	5.9 kcal/ml	2.1 kcal/ml

Figure 16. Heat of Combustion of Cyclohexane Derivatives

By comparing the heat of combustion of triquinoyl hydrate with that of six moles of carbon monoxide, the heat of polymerization and hydration of carbon monoxide may be estimated. The calculation is the following:

$$\frac{(6 \times 68) - 327}{6} = 13.5 \text{ kcal/mole of CO polymerized and hydrated}$$

The polymerization with hydration is thus an only slightly exothermic event.

Mass Spectrum

The electron impact mass spectrum of the ketone hydrate has been reported by Skujins, et al.[17] No parent ion was detected, but large yields of carbon dioxide, carbon monoxide and water were observed. Among other things, this observation leads to the prediction that the ketone hydrate will be sensitive to ionizing radiation and will release large amounts of gas when irradiated. No tests of radiation sensitivity have been performed, however.

Occasionally, deeply oxidized organic compounds are found to release elemental oxygen when decomposed. In the mass spectrum of triquinoyl hydrate and its cyclic homologs[17], there is a weak peak at m/e 16 and 32 as expected for elemental oxygen. This peak is still weaker in the less highly oxidized analogs tetrahydroxyquinone and rhodizonic acid[18]. The release of oxygen is only a minor decomposition pathway for triquinoyl hydrate in the mass spectrometer; carbon dioxide and water are the principal decomposition products.

Potentiometric Titration

Aqueous solutions of the ketone hydrate are acidic and may be titrated with aqueous base; the course of a potentiometric titration with sodium hydroxide is shown in Figure 17. The surprising result of this titration is that about two moles of base are required to neutralize one mole of the ketone hydrate. This result, according to Fleury and Fleury,[18] is due to the reaction

$$C_6H_{16}O_{14} + 2NaOH \longrightarrow NaOOC-\overset{\overset{\displaystyle OH}{|}}{C}=\overset{\overset{\displaystyle OH}{|}}{C}-\underset{\underset{\displaystyle OH}{|}}{CH}-COONa + CO_2 + 7H_2O$$
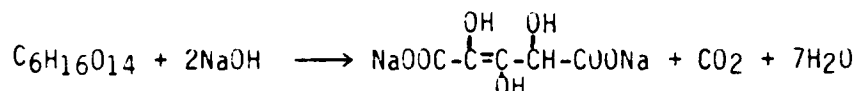
If this is the correct interpretation then the neutralization should be accompanied by an unusually large increase in entropy and in liquid volume due to 1) opening of the ring, 2) release of seven water molecules, and 3) release of carbon dioxide into the aqueous solution. The infrared spectrum of the solid residue remaining after evaporating the titrated solution showed that carboxylate groups are in fact present and that therefore ring opening does occur. The pK observed in the titration (Figure 17) gives further confirmation of the formation of carboxyl groups.

Ion Chromatography

Like many polyhydroxylic compounds, triquinoyl hydrate may be chromatographed on an acidic ion exchange resin with aqueous base as eluant; a pulsed amperometric detector may be used to monitor the electrochemically active components. When Aldrich Lot 1701 ML is chromatographed by a scheme of this kind[19], one large peak and several smaller, later emerging peaks are obtained (Figure 18). The chromatogram seems consistent with the finding of Fleury and Fleury that triquinoyl hydrate is immediately converted in 85% yield to NaOOC-C(OH)=C(OH)CH(OH)-COONa when dissolved in aqueous base. If the triquinoyl hydrate is heated at 65 C overnight nearly all of the triquinoyl hydrate is destroyed; peak 1 of the chromatogram is then smaller than later emerging peaks.

Instrument: Metrohm titrimeter

Electrode system: silver against calomel

Titrant: 0.1029 N sodium hydroxide

Solvent: water

Sample size: 0.1417 g

Equivalent weight, observed : 7.15 meq/g

Equivalent weight, calculated, assuming two acidic protons per molecule: 6.41 meq/g

pH at half neutralization: 5

end point 9.85 ml

Potential

Titrant added, ml
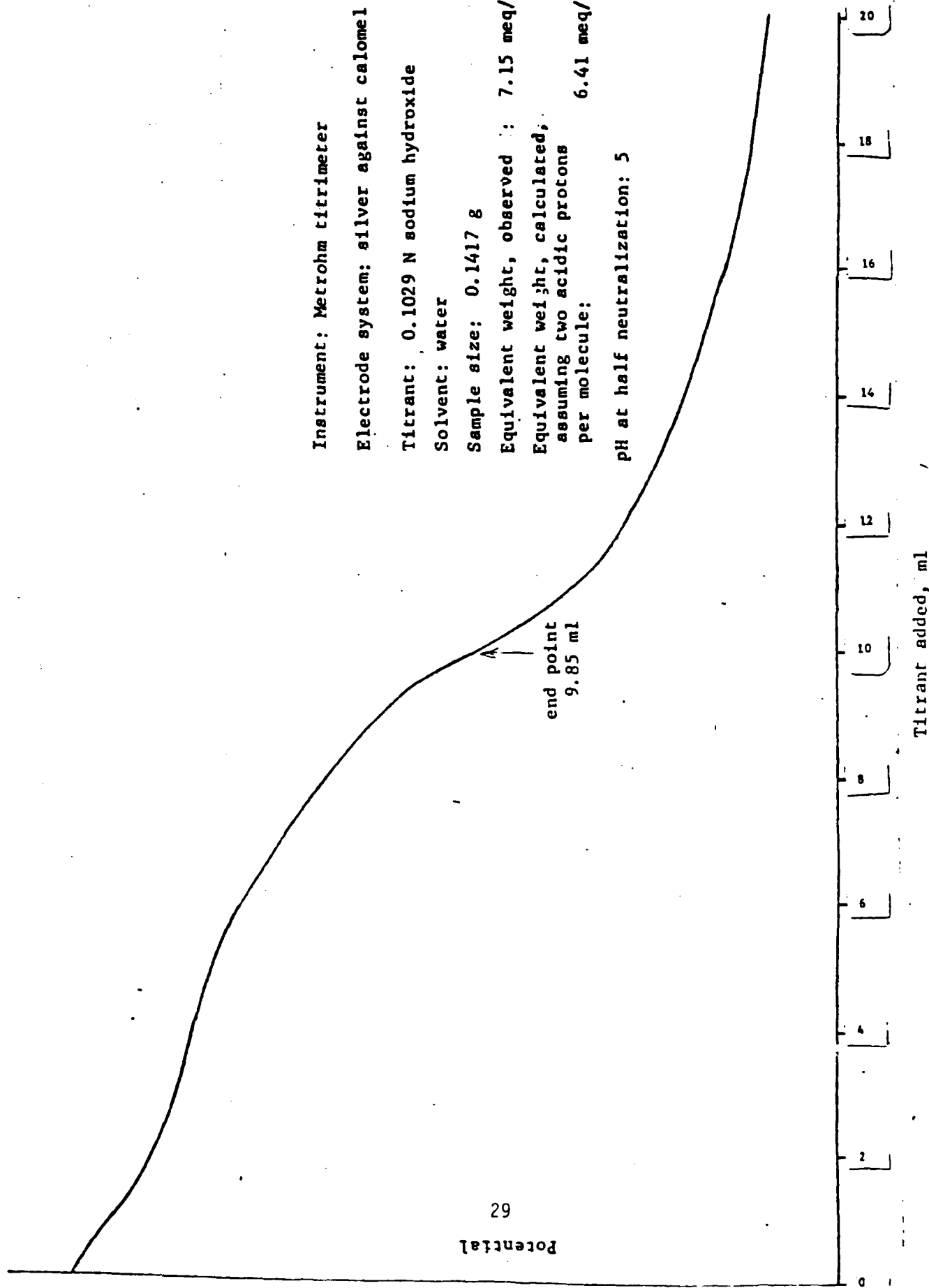
Figure 17. Potentiometric Titration of Triquinoyl Hydrate with Aqueous Sodium Hydroxide (Aldrich Lot 1701 ML)

29
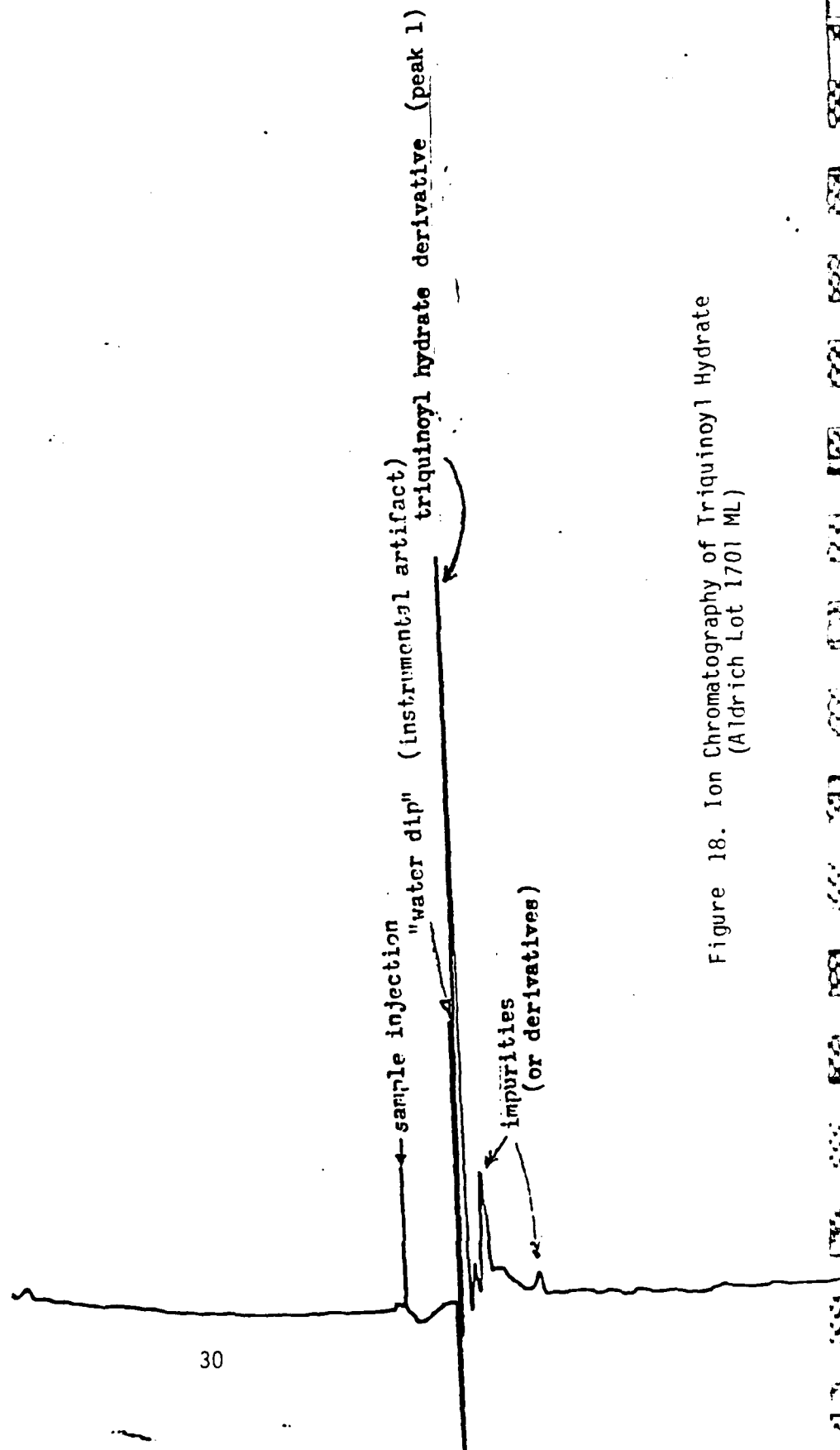
Figure 18. Ion Chromatography of Triquinoyl Hydrate
(Aldrich Lot 1701 ML)

Bill Edwards, Dionex Corporation, Sunnyvale, California provided the chromatogram of Figure 18.

Hardness

The high crosslink density and sharp crystal edges suggest that triquinoyl hydrate should have good abrasive properties. It has, in fact, been found that the crystal will scratch some of the harder organic solids -- polymethyl methacrylate, polystyrene, or cured epoxy resin. The melting point of the crystal is, of course, far lower than that of conventional inorganic abrasive materials and that melting point will place a low limit on the rate at which a hard substrate may be abraded with the ketone hydrate.

Detonability

Although some exothermic reactions may be envisioned for the gasification of hexaketocyclohexane octahydrate, all attempts at initiating the detonation were unsuccessful. Hammer blows, electrical discharges and flames all failed to initiate detonation. If detonation is possible, it will require an explosive charge to provide sufficient initiating impact.

The generalization has been made that organic dust explosions increase in destructive power as the carboxyl and hydroxyl content of the organic dust is increased[20]. Cellulose dust, for example, is more dangerous than polystyrene dust or coal dust. If the generalization about hydroxyl groups is correct, then triquinoyl hydrate is the most dangerous of organic dusts. No tests of the dust explosion hazard have been performed.

Pyrolysis

In an oven at 65 C and at 100 C the ketone hydrate loses weight rapidly (Figure 19) until about 50% weight loss is reached. The infrared spectrum of the gases collected over the samples shows that carbon dioxide and water are the major volatile products; carbon monoxide is not detected.

31
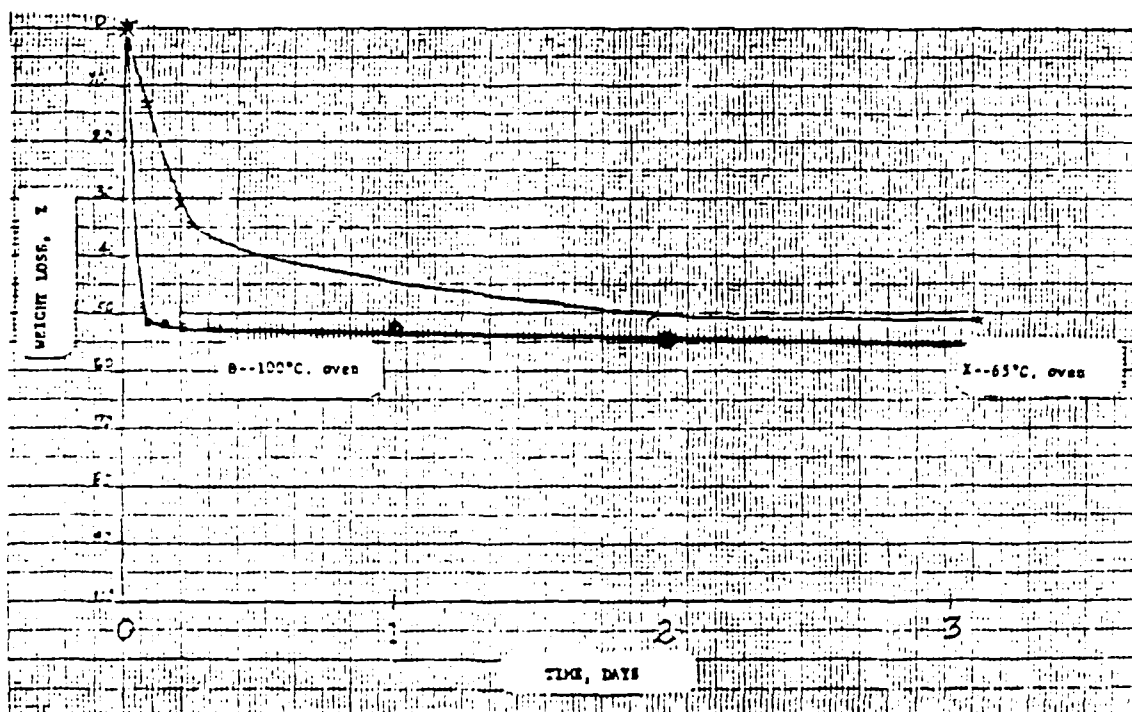
Figure 19. Rate of weight loss at two temperatures (triquinoyl hydrate, Aldrich Lot 1701 ML)

The solid residue remaining from this pyrolysis is a good reducing agent; it reacts vigorously with concentrated nitric acid. The pyrolysis process is therefore one of disproportionation in which the gases are the fully oxidized products and the solid residue is the reduced product.

In order to study the rate of decomposition at lower temperatures, samples were stored in Abderhalden drying pistols for long periods and withdrawn at intervals for weighing (Figure 20). Anhydrous calcium sulfate (Drierite) was charged to the drying apparatus to absorb the water released and the pistol was evacuated to accommodate carbon dioxide released. Except for the initial 5-6% weight loss attributable to loss of absorbed water, there is no evidence in the weight loss curves that the dehydration is a stepwise one. The evidence is rather that the initial loss of bound water from the crystal causes the entire network of hydrogen bonds to collapse and the water to evaporate. To put it another way, there is apparently no assembly of hydrogen bonds comparable in stability to that in the multiply-bonded network of Figure 11.

Solubility

Triquinoyl hydrate has some unusual properties. The dissolution of 10% of this solid in water at 25 C requires days of stirring; at 45 C dissolution is at least an order of magnitude faster. At 45 C dissolution in heavy water is much slower than in ordinary water. Adding a few percent of urea or sodium chloride to ordinary water increases the rate of dissolution at 25 C many fold. These effects can all be rationalized as being the result of exceptionally tight hydrogen bonding in the crystal.

Solubility of the ketone hydrate in cold aqueous acids is low -- its preparation and recrystallization from nitric acid depend on that fact. Dissolution in cold, concentrated sulfuric acid on the other hand is instantaneous and proceeds with evolution of gas. There is no charring as a result of the action of sulfuric acid as there is when carbohydrates are mixed with sulfuric acid. Perchloric acid (72%) is one of the better solvents; there is no obvious gas evolution during dissolution.

33

Figure 20.   Loss in Weight of Triquinoyl Hydrate
Heated Over Drierite at Reduced Pressure
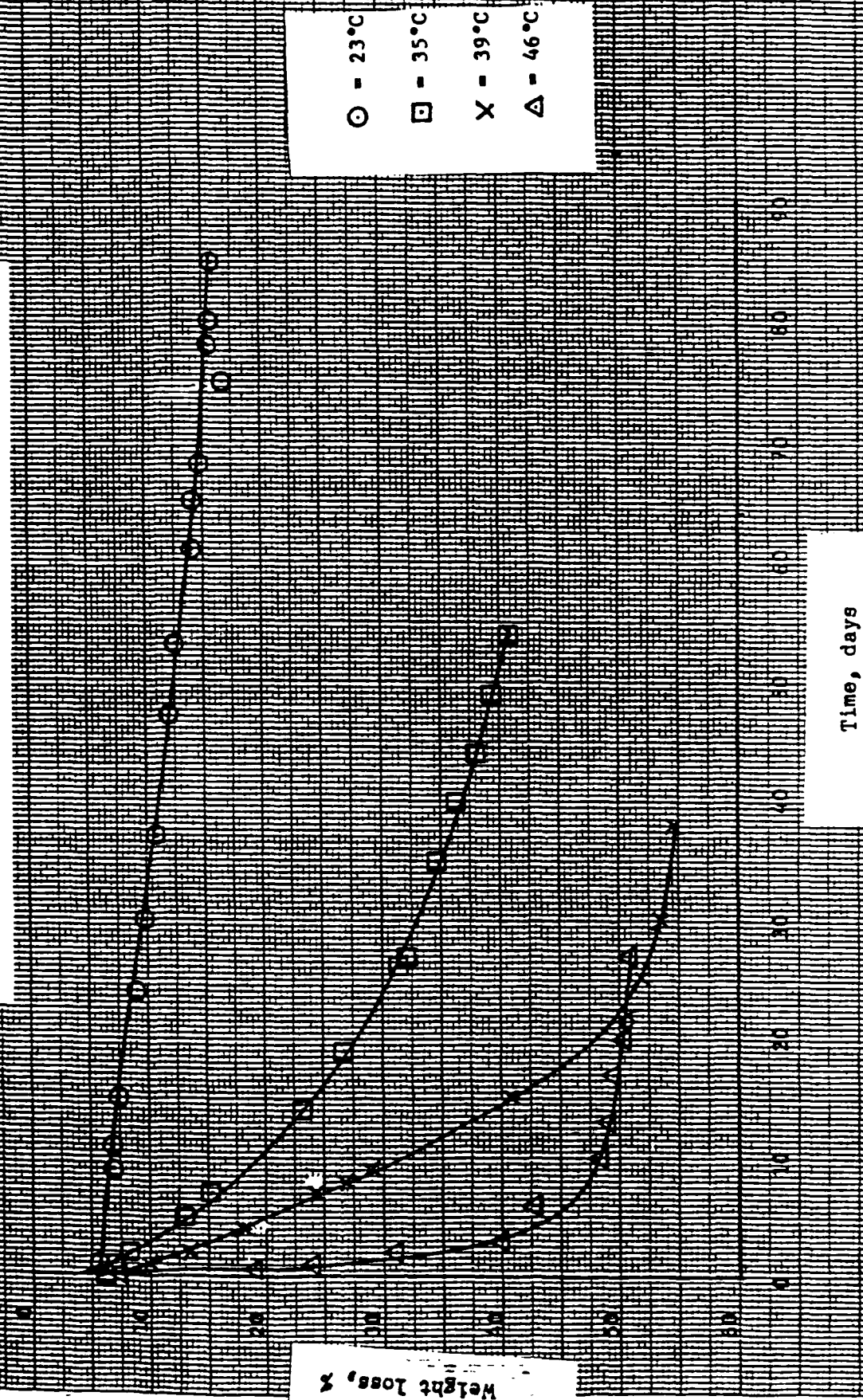
Few organic liquids are effective solvents. Methanol, ethanol or trifluoroethanol are ineffective; so also are tetrahydrofuran, nitromethane, acetonitrile and acetic acid. The strong "oxygen bases"[21] -- dimethylsulfoxide and dimethylformamide -- dissolve the compound rapidly but chemical changes accompany the dissolution.[22] Pyridine and other basic amines are also effective but these bases probably also attack the ketone hydrate chemically as aqueous bases do.

Figure 21 shows the weight increase for a sample of triquinoyl hydrate stored over water in a closed system. Weight of the sample increases steadily until eventually enough water is absorbed to dissolve the entire sample. If the solution obtained in this experiment is evaporated, essentially no triquinoyl hydrate is recovered. Good recoveries can be obtained, however, from solutions which are prepared in brine or in dilute acid.

Biological Activity

There are claims in the literature for remarkable biological activity in triquinoyl hydrate. It is said, for example, to promote the growth of yeast (Saccharomyces carlsbergensis), to attack the influenza virus or to assist diabetics in the metabolism of carbohydrates. Aldrich Chemical Company reports that there is a continuing steady demand for the material; it seems likely that such alleged biological activity is the reason for that demand.

The Aldrich material is labeled "Hazardous solid! Refrigerate! Avoid contact and inhalation!" The background leading to these warnings is not known. It seems likely however, that the hydrogen bonding power may allow the ketone hydrate to coagulate or restructure proteins. Caution seems in order until the absence of biological hazard is demonstrated. At least one closely related compound (chloral hydrate) is notorious for its physiological effect.

Figure 21. Gain in weight of triquinoyl hydrate stored over water. (Aldrich Lot 1701 ML)

36
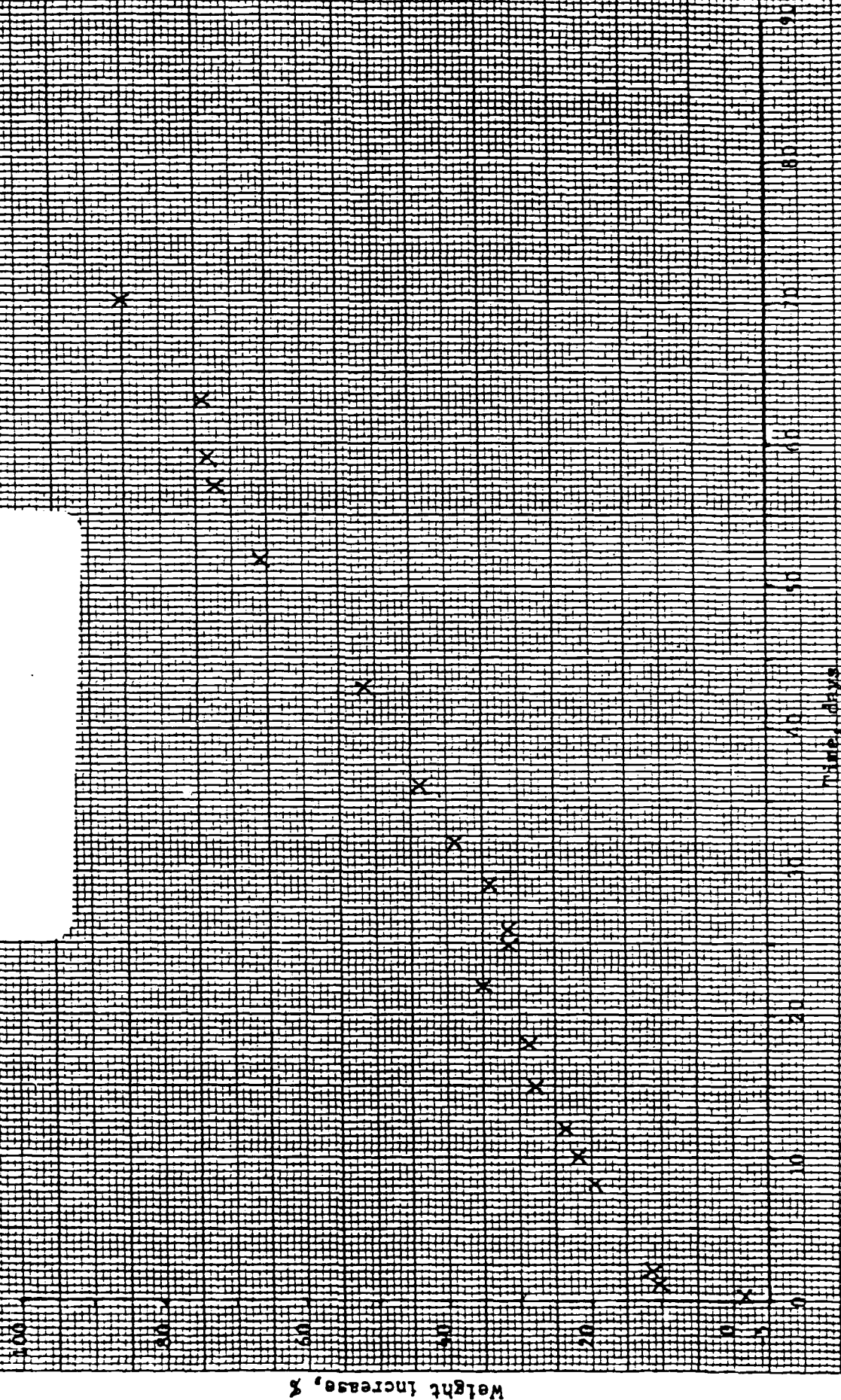
A HIGH MOLECULAR WEIGHT ANALOG

When graphite is treated at low temperatures with nitric-acid-based oxidizing agents, a solid graphite oxide[23,24] is obtained which resembles triquinoyl hydrate in several respects:

1) contains $C(OH)_2$ groups and puckered carbon rings
2) contains no carboxyl groups and no carbon-hydrogen bonds
3) has density 1.92 g/ml
4) swells or dissolves in aqueous base
5) releases water and carbon dioxide when heated
6) is a good oxidizing agent.

Triquinoyl hydrate may be regarded as the ultimate graphite oxide -- one containing the maximum oxygen-to-carbon ratio. In spite of its higher oxygen content, however, triquinoyl hydrate is not as effective as an oxidizing agent as is graphite oxide. The conversion of graphite oxide to graphite evidently provides a large driving force for the release of oxygen from graphite oxide.

DERIVATIVES

The elemental composition (Table 1), infrared spectrum (Figure 3) melting behavior (98-100 C) and ion chromatogram (Figure 18) of Aldrich Lot 1701 ML show that this sample of triquinoyl hydrate is of a purity adequate for preparative work. A large sample of this material was therefore put in storage in a minus 15 C freezer to preserve it for preparative experiments. These experiments are described in the following section.

Reaction with Benzyl Chloride

Treatment with benzyl chloride in pyridine is a standard method for preparing derivatives of carbohydrates. However, when triquinoyl hydrate was treated with this reagent (either two or ten moles of benzylchloride per mole of ketone hyrate) no ether-soluble product was obtained. The pyridine-induced dehydration/decarboxylation is evidently faster than benzylation.

Reaction with Butyl Isocyanate

A sample of triquinoyl hydrate was stored under butyl isocyanate at room temperature for a month. During that period there was no visible change in the triquinoyl hydrate.

Reaction with Trifluoroethanol

Triquinoyl hydrate was stored in trifluoroethanol containing some anhydrous copper sulfate to serve as a water detector. The mixture was allowed to stand at room temperature for one week; there was no change in the color of the copper sulfate.

Reaction with Hydrogen Peroxide

Triquinoyl hydrate dissolves promptly when mixed with excess 30% hydrogen peroxide solution at room temperature; heat and gas are released during the dissolution. Evaporation of the solution yields an acidic crystalline solid, m.p. 85-95 C, density 1.6-1.7 g/ml, absorbing strongly in the infrared at 1700 cm^{-1} and having the composition 27.23%C, 3.37%H, ash 1.70%. These results suggest that oxalic acid is the principal component of this mixture. Weight of the solid product is only 20% of the weight of the triquinoyl hydrate charged; most of the starting material is converted to water and carbon dioxide.

Reaction with Acetyl Nitrate

Acetyl nitrate ws prepared from acetic anhydride and nitric acid. To 0.3 gram of triquinoyl hydrate, one milliliter of acetyl nitrate was added. An immediate exotherm followed accompanied by vigorous gas generation. Methylene chloride was added, the mixture was stirred vigorously, the methylene chloride layer was separated, dried with magnesium sulfate and the methylene chloride evaporated in a nitrogen stream. The residue burned with difficulty and its infrared spectrum did not suggest the presence of nitrate esters. Any high-energy derivatives formed evidently decomposed during the initial exotherm.

Reaction with Oxidizing Acids

When mixed with 70% perchloric acid at room temperature, triquinoyl hydrate instantly dissolves. There is no obvious heat or gas evolution accompanying the dissolution and one gram of acid at 23 C will dissolve at least 0.14 grams of triquinoyl hydrate. The dissolution is remarkable for its rapidity; evidently perchloric acid breaks the hydrogen bond network in the ketone hydrate crystal quite promptly. Next to boric acid, perchloric acid is probably the best acidic solvent we have found for triquinoyl hydrate.

When the perchloric acid/triquinoyl hydrate solution is placed on a 250 C hotplate there is effervescence followed by a slow evaporation to dryness. No detonations have been obtained in several repetitions of this experiment. The solution retains its gas-generating capacity through several days of storage at room temperature. Even if triquinoyl hydrate is first heated overnight at 65 C to complete its disproportionation and then added to perchloric acid there is no immediate effervescence.

Nitric acid (70%) behaves quite differently toward the ketone hydrate. The solid $C_6H_{16}O_{14}$ may be stored under nitric acid for several days with little dissolution. However, if the acid is mixed with the 65 C disproportionation product there is instant vigorous effervescence. The ene-diol in the disproportionation product is evidently quite easily oxidized by nitric acid but not by perchloric. It may be possible to formulate a monopropellant that contains some perchloric acid (to dissolve the ketone hydrate) and some nitric acid (to trigger oxidation).

Carpenter and Fleury[25] reported that the dissolution of triquinoyl hydrate in 36 normal sulfuric acid is accompanied by release of carbon dioxide; this has now been confirmed. According to Carpenter and Fleury the other product of the decarboxylation is the aci-reductone:

$$HOOC-CHOH-\overset{OH}{\underset{OH}{C}}=C-COOH$$

39
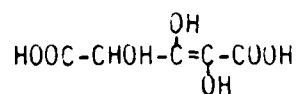
Reaction with a Diamine

When triquinoyl hydrate is mixed with an amine-terminated polyether, the ketone hydrate dissolves immediately and water vapor and carbon dioxide are released. (Both products are detected in the infrared spectrum of the vapor above the reaction mixture.) If the mixture is then heated at 100 C for a few hours it sets to a brittle glass. At the same time, there is additional loss of water. The spectrum contains the ether C-O stretch bands present in the ether starting material, the C-H stretch bands originally present and also stretch bands in the 6-7 micron region attributable to the generation of amide units. The product is probably a polyamide.

Reaction with Acetaldehyde

Triquinoyl hydrate was covered with freshly-distilled acetaldehyde and allowed to stand overnight at 5 C. Large crystals of acetaldehyde tetramer (metaldehyde) developed in the mixture. The tetramerization is also known to be catalyzed by formic acid, by sulfur dioxide or by hydrogen chloride -- obviously an acid catalyzed reaction. The acidity of the surface of triquinoyl hydrate is apparently high.

Reaction with Acetic Anhydride

Triquinoyl hydrate, 0.31 grams, was mixed with 2 ml of acetic anhydride and the mixture was allowed to stand in a closed tube for three days. There was no change in appearance during that period. A drop of pyridine was then added; a voluminous precipitate (presumed to be pyridinium acetate) formed immediately. A total of 1.1 grams of pyridine was then added with continuous mixing. The mixture was centrifuged to remove the solid phase; the supernatant liquid was added to 10 ml of petroleum ether to give a system containing two liquid phases. The lower phase was separated, washed with additional petroleum ether, concentrated in a stream of nitrogen and dried overnight at reduced pressure over sodium hydroxide to give 0.12 grams of residue. The residue had a nondescript infrared spectrum, and failed to crystallize in several days standing.

Reaction with Thionyl Chloride

When the ketone hydrate is allowed to stand in thionyl chloride at room temperature, sulfur dioxide and hydrogen chloride are released steadily for a period of days and rhodizonic acid accumulates in the solid mixture. (The reduction of the ketone hydrate by sulfur dioxide is a known reaction.[26,27,28]) This may be a useful method for preparing fully dehydrated rhodizonic acid.

Reaction with Diepoxides

1) A mixture of vacuum-dried triquinoyl hydrate with an equal weight of the diglycidyl either of bisphenol A was heated at 40 C for seven days. Weight loss during this period was only 0.4%. During the heating period resin cure advanced only slightly.

2) In another experiment the same mixture was heated at 65 C for 40 hours. During that period the mixture was converted to a rigid gel (chloroform insolubles $\geq$ 95%). The infrared spectrum indicated that both the triquinoyl hydrate and epoxy groups were consumed during the cure. Weight loss during cure was 20%.

3) Triquinoyl hydrate, 0.38 grams, was mixed with 1.91 grams of the diepoxide of vinylcyclohexene and the mixture was heated at 40 C for five days. The liquid diepoxide was converted to a void-free glass. Most of the triquinoyl hydrate remained at the bottom of the reaction vessel, undissolved and apparently unchanged. Weight loss during the cure was only 0.2%. When stored for an additional two months at 40 C the mixture retained its original appearance and lost only 4% in weight (Figure 22). Gassing of triquinoyl hydrate at 40 C is clearly suppressed by covering the ketone hydrate with this liquid diepoxide.

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Figure 22. Weight of a Triquinoyl Hydrate/UNOX 206 Mixture
Stored at 40 C

Weight Loss, %

Time, days
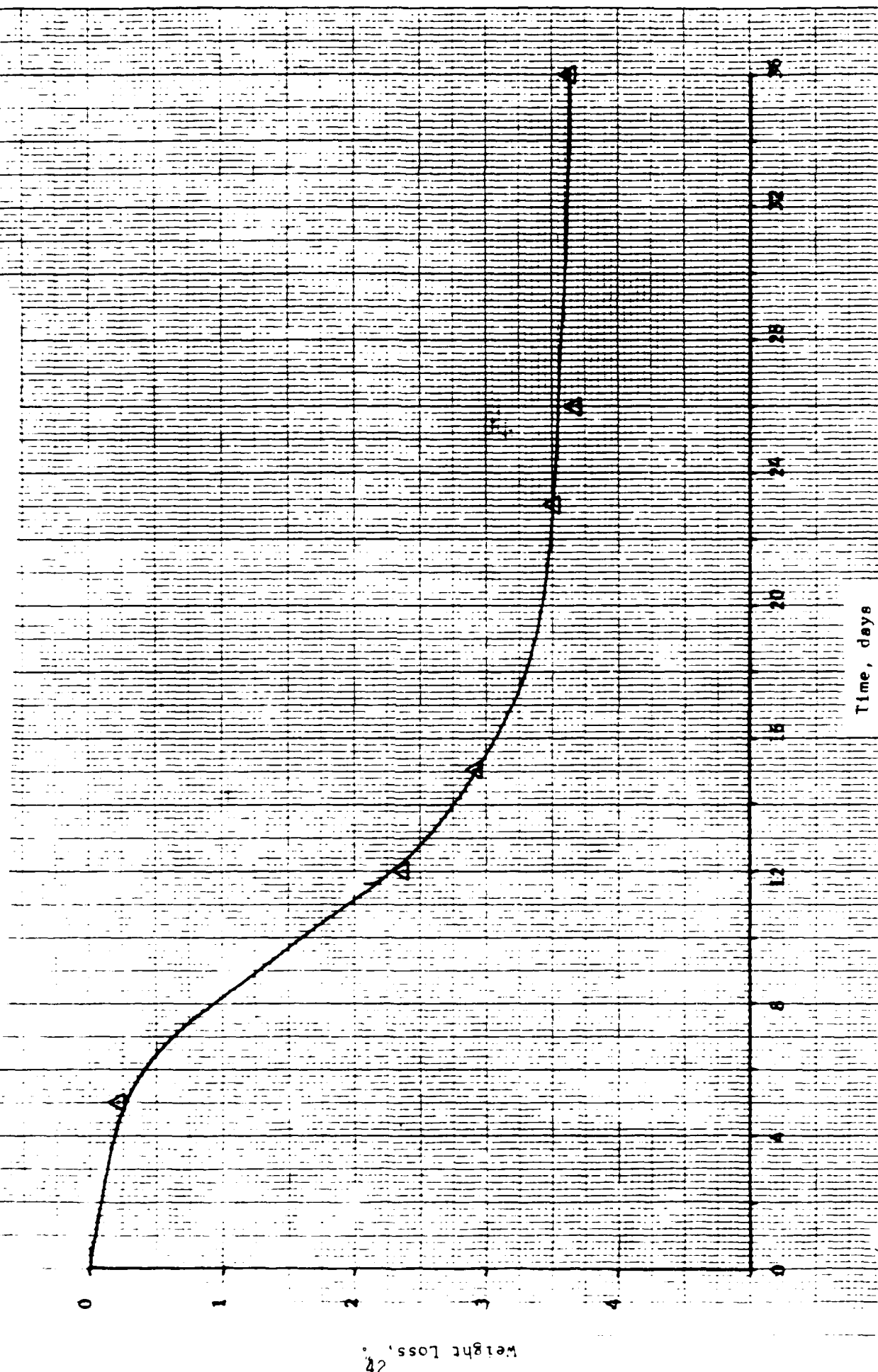
4) In another experiment the same mixture was heated overnight at 65 C. During that period the reaction vessel was filled to overflowing with a brittle, highly expanded, chloroform-insoluble foam. The infrared spectrum of the cured foam indicated that both triqinoyl hydrate and epoxy groups were consumed during the 65 C heating.

5) In another experiment, triquinoyl hydrate was mixed with 10% of its own weight of the diepoxide of vinylcyclohexene and stored in an open vial at 40 C. Weight loss in two months was 8%; without the added diepoxide a weight loss of 50% is expected (Figure 20; also see Figure 23).

6) When heated alone at the temperatures indicated neither of the epoxy monomers polymerize.

Vinylcyclohexene diepoxide is known to polymerize in the presence of acids while diglycidyl ethers are somewhat less sensitive to acids[29]. The suspicion therefore arises that the polymerizations described above are associated with the acidity of triquinoyl hydrate. Other acid-sensitive monomers are also polymerized by triquinoyl hydrate: -caprolactone changes to a more viscous liquid if heated at 65 C with triquinoyl hydrate, and acetaldehyde deposits (metaldehyde) if stored at 5 C for several hours over triquinoyl hydrate. Other acid-sensitive monomers (furan, ethyl vinyl ether, isoprene, myrcene, epichlorohydrin, propylene oxide) are not visibly affected by contact with triquinoyl hydrate at 25 C. Water released from the ketone hydrate is perhaps an inhibitor of those polymerizations.

Triquinoyl Hydrate as a Polymerization Inhibitor

A styrene/methyl methacrylate mixture polymerized without added initiator when stored a few days at 65 C; a sample containing triquinoyl hydrate did not polymerize. AIBN was then added to the triquinoyl hydrate-containing sample; the mixture polymerized in a few hours. A sample of methacrylic acid did not polymerize when stored at 65 degrees with triquinoyl hydrate present or absent. When AIBN was added, both polymerized rapidly.

Figure 23. Weight of a Triquinoyl Hydrate/10% UNOX 206 Mixture
Stored at 65 C

Weight Loss, %
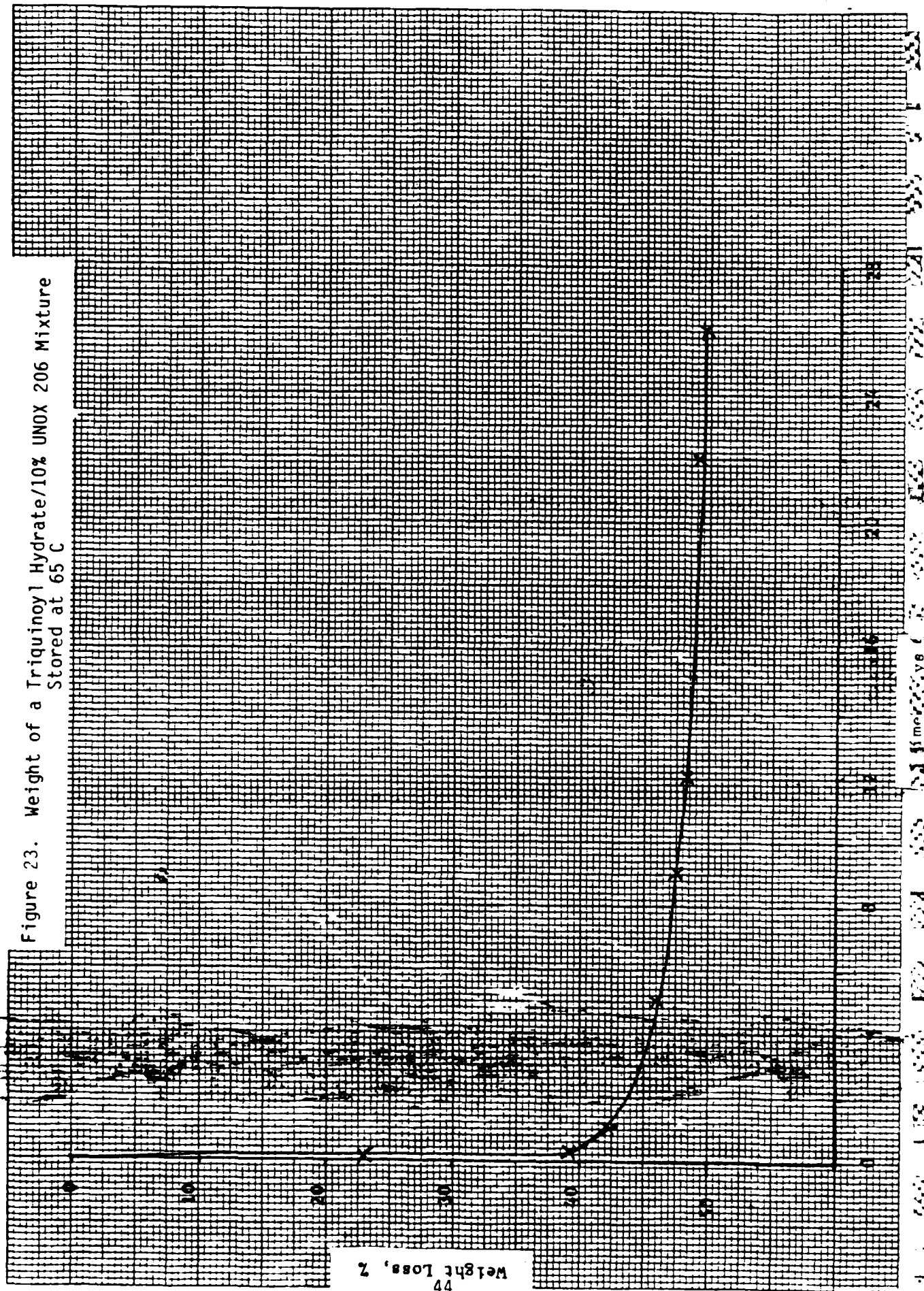
Failure of hexaketocyclohexane octahydrate to initiate vinyl polymerization suggests that the decomposition of the ketone hydrate at 65 C does not proceed through free radical intermediates. The decomposition may be concerted (like some decarboxylation reactions) or have an ionic character.

Reaction with Hydroxylamine

The presence of free ketone in an aqueous solution of ketone hydrate suggested that conversion to an oxime might be possible. It is known that treating leuconic acid with aqueous hydroxylamine hydrochloride does in fact convert that material to a pentoxime.[30] The ketone hydrate was therefore treated at 40 C with a large excess (100 moles/1 mole) of hydroxylamine hydrochloride (saturated aqueous solution). The reaction mixture was analyzed at intervals by thin layer chromatography (silica plates developed with methanol).

After a few hours of reaction time a blue material formed in the reaction mixture detected as a spot at R_f = 0.6 - 0.7 on silica chromatography plates. The material in this spot has the following properties:

1) Located on TLC plate at same R_f as hydroxylamine hydrochloride.
2) Soluble in water or methanol but not in ether, heptane or methylene chloride.
3) Stable in air at 25 C for weeks but disappears from the chromatogram when the plate is heated for a few hours at 100 C.
4) Requires very high hydroxylamine hydrochloride/ketone hydrate ratio for formation (more than six to one).
5) Hydrolyzed under mildly basic or mildly acidic conditions.
6) Not changed in color by spraying with aqueous nickel chloride (oximes probably absent), with 2-4-dinitrophenylhydrazine (ketones probably absent), with silver nitrate + sodium hydroxide (oxidizable structure absent), with aniline (nitroso structures probably absent), or potassium tri-iodide (oxidizing structures absent).

7) Not formed by treating the ketone hydrate with sixteen assorted acidic reducing agents other than hydroxylamine hydrochloride (sodium bisulfite, stannous chloride, etc.).

8) Rate of its formation increases rapidly with increasing triquinoyl hydrate concentration.

The identity of this derivative is not yet established. Some possibilities are that 1), it is the condensation product of cyclic polyketone, reduced cyclic polyketone and ammonia, (like Ruhemann's purple)[31], or 2) it is a cyclic polyketone (1,1,2,2-tetramethylcyclopentane trione is blue)[32].

Reaction with Semicarbazide

Several experiments have been performed in which hexaketocyclohexane octahydrate was treated with hydrazine, semicarbazide or carbohydrazide. The following is one of the most informative of those:

> To a solution containing semicarbazide hydrochloride (0.67 g, 0.006 mole), sodium acetate (1.00 g, 0.012 mole) and water (3 ml) there was added an equivalent quantity of triquinoyl hydrate (0.31 g, 0.001 mole). The ketone hydrate dissolved immediately and the solution turned red-brown within a few minutes. The mixture was allowed to stand in a stoppered tube for a week then was evaporated to dryness -- first under a stream of nitrogen, then in a desiccator over sodium hydroxide pellets then at reduced pressure over sodium hydroxide (to remove acetic acid). During the final drying some crystalline material separated from the gummy residue. The infrared spectrum on the gum residue showed that the ketone hydrate charged was consumed completely (no 875 cm^{-1} band). The thin layer chromatogram of the gum when developed with iodine vapor showed presence of at least one iodine-reducing

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material; the R_f of this material suggested that it was unreacted semicarbazide rather than the hexa(semicarbazone). Total weight of the dried residue was 1.48 grams; theoretical residue weight for complete conversion to hexa(semicarbazone) with loss of fourteen moles of water and six of acetic acid, is 1.35 grams.

One gram of this reaction product was then extracted three times with methanol to yield 0.6 grams of methanol-soluble material. That material was then dissolved in 50 ml of water and passed through a bed of mixed cationic/anionic ion exchange resin to remove all ionic components. Evaporation of the de-ionized aqueous solution gave 0.07 gram of solid products, melting point 230-235C. Thin layer chromatography on this product showed two major components were present (R_f = 0.8 - 0.9); neither reduced iodine. The infrared showed no C-H stretch, strong 3200 and 3400 cm^{-1} and strong 1700 cm^{-1}. Elemental composition of product: C 26.81%, C 5.27%, N 34.29%, O (by difference) 33.63%.

These results are interpreted as follows: 1) semicarbazide, like urea, facilitates the dissolution of the ketone hydrate in water; semicarbazide is probably another good hydrogen-bond breaker. 2) The red color which develops is a familiar one -- it is due to rhodizonic acid, the first reduction product of the ketone hydrate. 3) Reaction is quite slow; the condensation of semicarbazide with ketone hydrate is at least an order of magnitude slower than with cyclohexane. The week-long reaction period is justified. 4) Most of the reaction products are ionic (removed by mixed cationic/anionic ion exchange resin). These are products of ring opening reactions of triquinoyl hydrate.

Photochemistry

Solid triquinoyl hydrate may be exposed to 254-nm radiation from a low pressure mercury arc for many hours with no visible change and no change in infrared spectrum. Similar results are obtained when an aqueous slurry or a slurry in 1 N HCl is irradiated. However, if a light-sensitive, water-soluble cyano complex such as potassium octacyanomolybdate is

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dissolved in water and triquinoyl hydrate is slurried in that solution then a light-sensitive mixture results. The light-induced photoaquation[33] of the cyano complex evidently releases enough cyanide ion to render the solution basic; the triquinoyl hydrate dissolves quickly in an equivalent amount of aqueous cyanide solution. In this way a light-triggered volume increase can probably be attained.

APPLICATIONS

The properties and chemical reactions of triquinoyl hydrate have suggested a number of uses for this compound. These are described in the following sections.

Cool Gas Generator

The low heat of combustion, high density, non-corrosive and non-toxic nature of the gaseous decomposition products, and the high heat of fusion/evaporation all argue for this use of triquinoyl hydate. The cool gases resulting from burning a triquinoyl hydrate/oxidizer mixture might be used to drive turbines, inflate airbags and liferafts or to break fasteners.

Monopropellant Ingredient

The solubility of triquinoyl hydrate in concentrated perchloric acid suggests using this solution as a liquid monopropellant. As the solvent and oxidizing component perchloric acid stronger than the usual 70% may be required.

Agent for Driving Hydraulic Machinery

The large entropy change associated with the release of seven moles of water, one of carbon dioxide and the opening of the triquinoyl ring should allow the development of high pressure in closed, water-filled hydraulic systems. Reaction could be brought about photochemically or by adding base. To get maximum increases in pressure the ketone hydrate should be

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stored in a hydraulic system as the solid. Possible applications would be in the opening of rock strata (as in secondary oil recovery) and in the forming of metal with hydraulic apparatus.

Comonomer for Condensation Polymerization

The ring-opening reaction of triquinoyl hydrate with diamines yields a non-crystalline polyamide which should adhere well to high-energy surfaces such as wood, glass or metal.

Low-loss Dielectric

The rigidity of the hydrogen-bonded network indicated by the x-ray diffraction pattern suggests that the mica-like triquinoyl hydrate platelets will suffer less dielectric loss than other crystalline carbohydrates (such as paper) when placed in an oscillating electric field.

Curing Agent for Epoxy Resins

Triquinoyl hydrate functions as a curing agent for liquid diepoxides, especially those of the epoxidized olefin type. At elevated temperatures it simultaneously releases gas, thus generating a cured-in-place epoxy foam, possibly of interest as thermal insulation.

SYNTHETIC ROUTES TO TND

The basic synthetic scheme laid out for preparation of TND, shown in Figure 24, is based the work of Begland[4]. In that paper, preparation of each of the amino-cyano diazines from reaction of diaminomaleonitrile (DAMN) and diiminosuccinonitrile (DISN) under varying reaction conditions is described in some detail. Conversion of tetracyanodiazine to 2,6-diamino-3,5-dinitrodiazine is described by D.S. Donald.[5] Hydrolysis of tetracyanodiazine followed by nitrolysis of the tetra-acid is the most direct route to TND, but investigation of the other three approaches promised to be more interesting because of the observations that could be made during a study of the amine oxidations.

DISN was prepared from the commercially available DAMN by oxidation with dichlorodicyanobenzoquinone.3 DAMN and DISN reacted with 1 equivalent of sulfuric acid in tetrahydrofuran (THF) to give 2-amino-3,5,6-tricyano-diazine as reported by Begland[4]. Hydrolysis of this to the triacid was accomplished by heating in 5N sulfuric acid for 3 days. Reaction of DAMN and DISN in trifluoroacetic acid provided the tetracyanodiazine in good yield, and hydrolysis to the tetra-acid in sulfuric acid proceeded as described. Several attempts to prepare 2,3-diamino-5,6-dicyanodiazine by reaction of DAMN and DISN in acetonitrile failed.

A number of attempts were made to nitrolyze diazine tetracarboxylic acid and 2-amino-3,5,6-tricarboxydiazine to the corresponding nitrodiazines. Initially, the procedure reported for preparation of 2,6-diamino-3,5-dinitrodiazine[5] was employed. When this method (reaction in nitric and sulfuric acids at ambient temperature) gave no reaction in either case, the reaction temperature was increased in a stepwise fashion to 60 C, and the reaction time was extended to several hours. As the temperature was increased from 25 C to 60 C, less and less of the starting material was recovered. After 3 hours at 60 C, neither the starting material nor any detectable product could be found. An attempt to affect nitrolysis in a mixture of nitric acid and acetic anhydride at the boiling point of the reaction mixture resulted in recovery of the starting material.
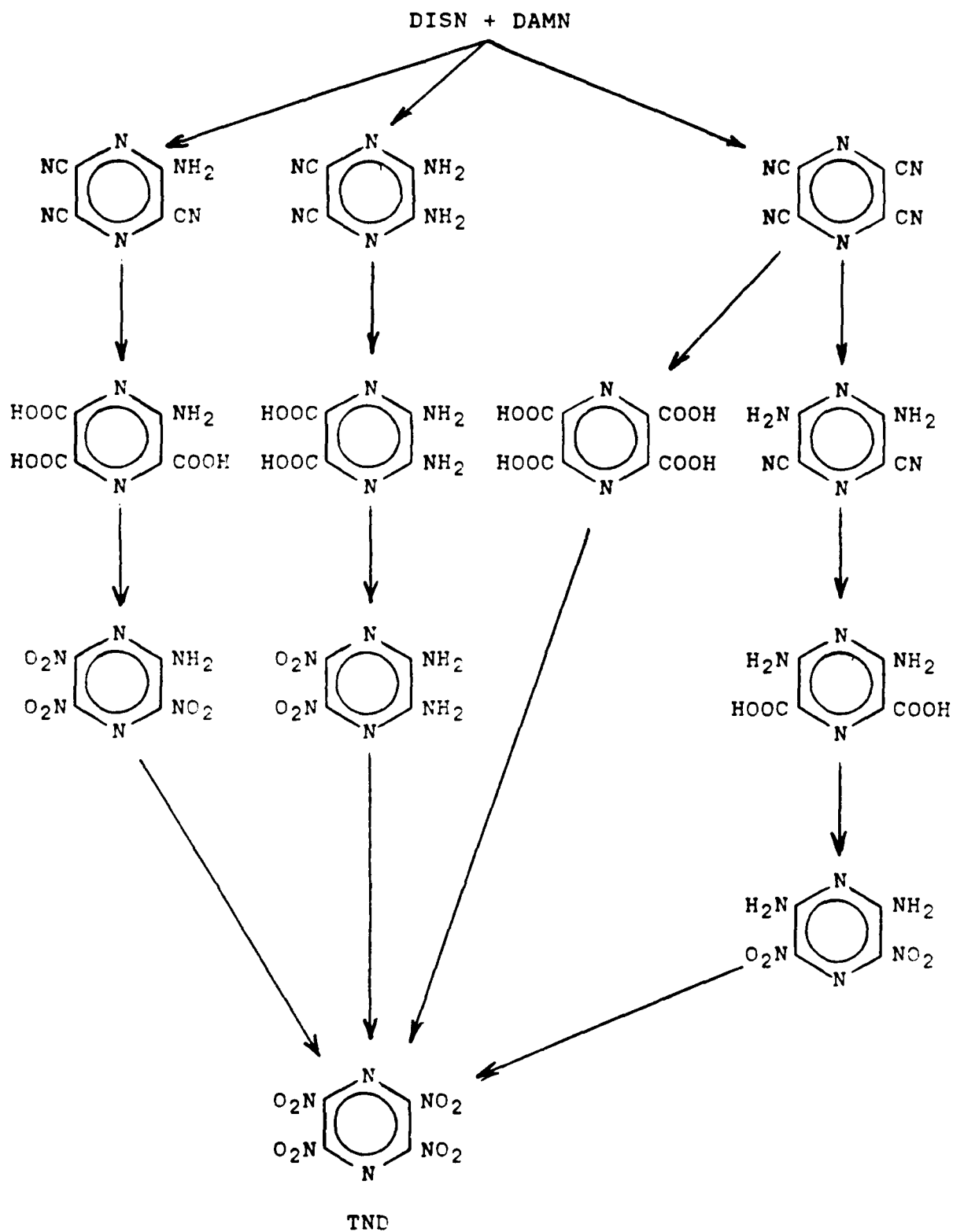
Figure 24. Synthetic Routes to TND

Since the three most direct routes to TND in Figure 24 were unsuccessful, we began working on the fourth route through 2,6-diamino-3,5-dinitrodiazine. Based on D. Donald's patent,[5] tetracyanodiazine in THF was reacted with liquid ammonia to yield 2,6-diamino-3,5-dicyanodiazine which was then hydrolyzed to 2,6-diamino-3,5-dicarboxydiazine with 5% sodium hydroxide. Nitrolysis of this diacid in a mixture of nitric and sulfuric acids gave 2,6-diamino-3,5-dinitrodiazine. Our efforts to oxidize this compound to TND is described in the next section of this report.

When we were unable to prepare 2,3-diamino-5,6-dicyanodiazine from the reaction of DAMN and DISN, an alternative route was sought. K. Mitsuhashi[34] described it's synthesis as shown in Figure 25. 2,3-dioxo-5,6-dicyano-1,2,3,4-tetrahydrodiazine was prepared by reaction of DAMN with oxalyl chloride in dioxane as reported, but the experimental procedure was complicated by the extremely exothermic solvation of oxalyl chloride in dioxane. We found that the reaction could be carried out in methylene chloride at reflux over a period of 5 hours. The solid complex of oxalyl chloride and dioxane was avoided and methylene chloride could be removed from the final product more readily than dioxane because of the lower boiling point.

We were unable to reproduce Mitsuhashi's method of preparing 2,3-dichloro-5,6-dicyanodiazine using phosphorusoxychloride. Several attempts resulted in recovery of only dark tars. An alternative route using thionyl chloride as described by D. Donald[35] was successful.

Conversion of 2,3-dichloro-5,6-dicyanodiazine to 2,3- diamino-5,6-dicyanodiazine by the method of Mitsuhashi was successful. Ammonia was bubbled through a solution of the dichlorodiazine in dimethylformamide (DMF) at -10 C until saturated. After evaporation of the DMF, the product was recrystallized from acetone.

DAMN + ClCOCOCl $\longrightarrow$ $\longrightarrow$ $\longrightarrow$

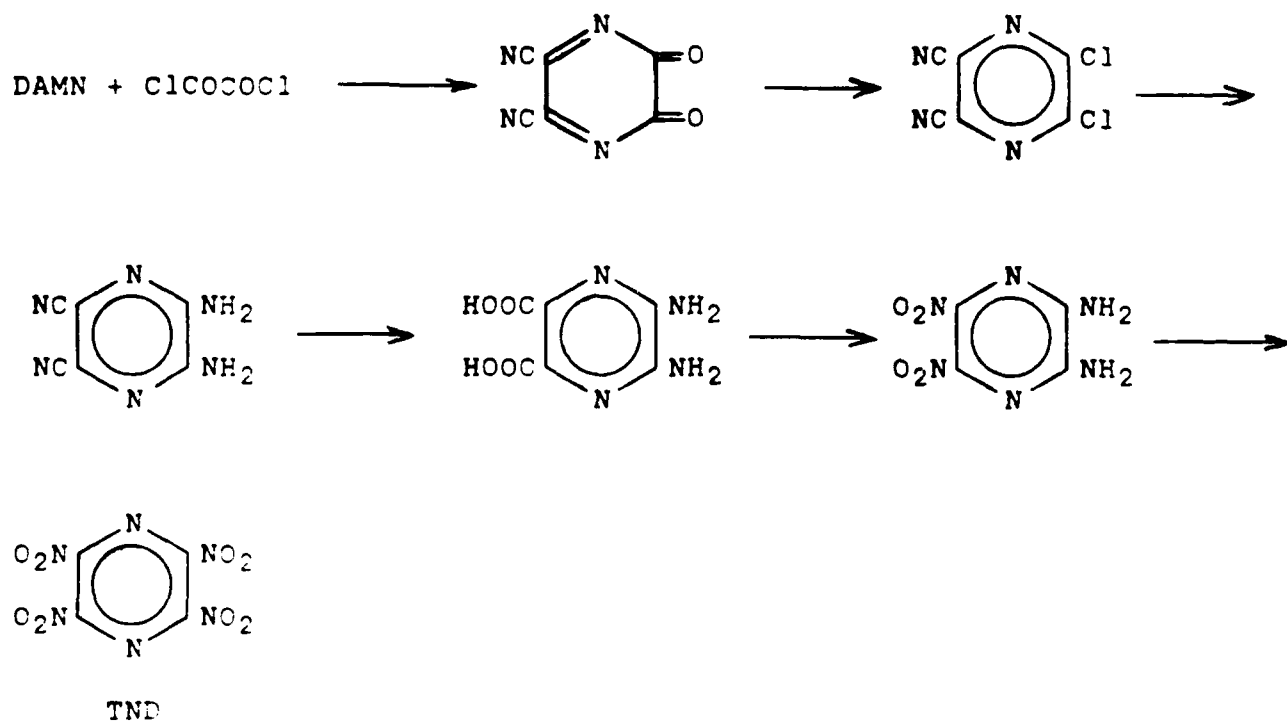 $\longrightarrow$ $\longrightarrow$ $\longrightarrow$

TND

Figure 25. Alternative Synthesis of 2,3-Diamino-5,6-dinitro-1,4-diazine

Finally, 2,3-diamino-5,6-dicyanodiazine was hydrolyzed to the corresponding diacid by refluxing in 5% sodium hydroxide for 5 days followed by acidification and filtration of the product. Nitrolysis of the diacid yielded 2,3-diamino-5,6-dinitrodiazine which was subjected to a number of oxidation procedures in an attempt to prepare TND.

OXIDATION OF DIAMINODINITRODIAZINES

The final step in the synthesis of TND was oxidation of either of the two diaminodinitrodiazines. At the beginning of this work it was anticipated that the two isomers would respond differently to the various oxidative procedures to be attempted. 2,6-Diamino-3,5-dinitrodiazine provides an arrangement of atoms which would lend itself to forming strong intramolecular hydrogen bonds, Figure 26. In the case of the 2,3-diamino isomer, no such bonding is possible, although intermolecular bonding can occur.
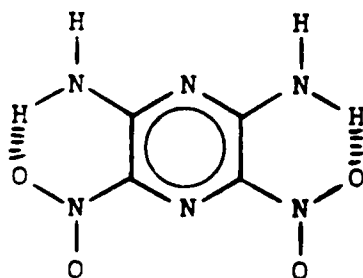

Figure 26. Hydrogen Bonding of 2,6-Diamino-3,5-dinitro-1,4-diazine

For both of the isomers, it was clear that oxidation would be difficult because of the presence of the nitro groups already there.

Our initial investigation of oxidative methods began with a relatively mild reagent, m-chloroperbenzoic acid. This has been used previously in the

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oxidation of both aminobenzoquinones and aminotetrazines.[2] Since the reaction is somewhat temperature dependent, an attempt was made in refluxing chloroform, and when that failed, the temperature was raised by using 1,2-dichloroethane as the solvent. In all of the oxidation attempts using m-chloroperbenzoic acid the starting material was recovered in near quantitative yield.

Peroxytrifluoroacetic acid has been used to oxidize several substituted anilines.[36] When a solution of either of the two aminodiazine isomers in trifluoroacetic acid was treated with hydrogen peroxide, only the starting material was recovered. The reaction was carried out by adding the peroxide to the reaction mixture at 60 C, and then stirring for 18 hours at ambient temperature.

Hydrogen peroxide in fuming sulfuric acid has been used to prepare hexanitrobenzene from pentanitroaniline.[37] Prior to the application of this method, pentanitroaniline had been resistant to oxidation by many different procedures and reagents. Treatment of each of the aminodiazines with hydrogen peroxide in 30% fuming sulfuric acid resulted in recovery of the starting materials.

A similar reagent, peroxytrifluoromethane sulfonic acid, can be prepared and reacted in the same way as peroxytrifluoroacetic acid. It has also been used in the preparation of hexanitrobenzene.[38] Again, treatment of both of the isomers led to recovery of the starting material.

Nielsen[38] also used a potassium persulfate in trifluoromethane sulfonic acid to oxidize pentanitroaniline to hexanitrobenzene. Treatment of both of the diaminodiazine isomers resulted in recovery of the starting material.

A variety of substituted anilines have been oxidized by passing ozone over the substrate impregnated on dry silica gel.[39] The materials that were studied were readily soluble in an organic solvent which could be evaporated after the coating process. In the case of the diaminodiazines, limited solubility in appropriate solvents made it difficult to assure good coating of the silica gel. Several attempts to oxidize each of the isomers at varying temperatures and employing a large excess of ozone gave no indication that any oxidation had occured.

In an attempt to provide more intimate contact between the substrates and ozone, direct oxidation in fluorotrichloromethane[40] was attempted. Again, there was no indication of any oxidation.

EXPERIMENTAL

The detailed experimental procedures reported here are presented because they describe the synthesis of new compounds or because they represent substantially modified methods of preparing previously known compounds.

2,3-Dioxo-5,6-dicyano-1,2,3,4-tetrahydrodiazine

A solution of 25 g (0.197 mol) of oxalyl chloride in methylene chloride was added to a solution of 21 g (0.194 mol) of diaminomaleonitrile in 200 ml of methylene chloride with stirring at ambient temperature. The reaction mixture was refluxed for 5 hours, cooled to room temperature, and the product was removed by filtration. The product was recrystallized from water yielding 22.5 g (72%). mp 270 C.

2,3-Diamino-5,6-dicarboxy-1,4-diazine

2,3-diamino-5,6-dicyanodiazine, 22.5 g (0.118 mol), was suspended in 500 ml of 5% sodium hydroxide and refluxed for 6 days. The dark solution was added to 1500 ml of water at 50 C, and 150 ml of concentrated hydrochloric acid was added dropwise with efficient stirring. After cooling the solution, the tan solid was removed by filtration, washed with cold water, and dried to yield 23 g of product (98%).

2,3-Diamino-5,6-dinitro-1,4-diazine

To 120 ml of concentrated sulfuric acid at 10 C was added 23 g (0.116 mol) of 2,3-diamino-5,6-dicarboxydiazine in small portions while maintaining the temperature at 10 to 15 C. A previously prepared mixture of 15 ml of concentrated nitric acid and 15 ml of concentrated sulfuric acid was added dropwise at 10 C. The reaction mixture was allowed to warm to room temperature and stir for 3 hours. Gas evolution began during the warming process and continued throughout most of the reaction period. The reaction

mixture was poured slowly onto 2000 ml of ice/water, stirred for 30 min, and then filtered. The product was washed with a small amount of cold water and dried in a vacuum to yield 9.9 g (43).

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GLOSSARY

DAMN	Diaminomaleonitrile
DISN	Diiminosuccinonitrile
DMF	Dimethylformamide
DNTT	3,6-Dinitro-1,2,4,5-tetrazine
HMX	Cyclotetramethylenetetranitramine
RDX	Cyclotrimethylenetrinitramine
THF	Tetrahydrofuran
TND	2,3,5,6-Tetranitro-1,4-diazine
TTZ	2,4,6-Trinitro-1,3,5-triazine

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